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Process Sources

IT Enviroscience
Knoxville, TN

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EPA is developing new source performance standards under Section 111 of the Clean Air Act and national emission standards for hazardous air pollutants under Section 112 for volatile organic compound emissions (VOC) from organic chemical manufacturing facilities. In support of this effort, data were gathered on chemical processing routes, VOC emissions, control techniques, control costs, and environmental impacts resulting from control. These data have been analyzed and assimilated into the ten volumes comprising this report.

This volume covers the following process emission sources within organic chemical plants: air oxidation reactions, reactions involving carrier gases, vacuum producing systems, sulfuric acid recovery operations, and process upsets.

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Organic Chemical Manufacturing
Volume 2: Process Sources

Emission Standards and Engineering Division

U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Air, Noise, and Radiation
Office of Air Quality Planning and Standards
Research Triangle Park, North Carolina 27711

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REPORT 1

THE GENERIC STANDARD APPROACH

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I. THE GENERIC STANDARD APPROACH

A. CONCEPT DEVELOPMENT

The synthetic organic chemicals industry is estimated to produce 350 to 400 chemicals by about 600 processes. For processes used to manufacture the same products, differences in the catalysts, reaction conditions, separations, product purity, reactant type and purity, types of storage, waste treatment, and company process design philosophy all affect the specific design, performance, and emissions at the individual production site.

The standard approach to the control of volatile organic compounds (VOC) in the organic chemicals industry consists of identification of the major emission-producing processes and generation of industry-wide regulations for manufacturers of specific products, e.g., VOC regulations for manufacturers of formaldehyde, acrylic acid, and others. This is the standard approach normally required by EPA for the collection of emission and control-device performance data to generate support documents for VOC New Source Performance Standards (NSPS). In this approach the major advantages are that the emission sources common to all manufacturers of that product are highlighted and investigated. Data from this effort allow the regulatory agency to estimate the volume and composition of the emissions from plants producing a common chemical and to estimate the cost effectiveness of various control devices on that common emission.

Unfortunately, the many plant-to-plant variations that exist can still cause significant variations in the organic emissions of existing plants. Some 400 to 600 product regulations would be necessary to completely cover the industry, and sensitive data are required to assure that the regulation applies to all the manufacturers of a specific product. If regulations could be developed for existing products, more of them would be needed for the steady stream of new products; also, technology changes in the forthcoming years would make many of these current product standards obsolete.

The growing realization that it is impossible to apply the normal product standard approach to regulating process emissions from SOCMI substantiates the belief that the generic approach is the only approach that is applicable and sustainable. The starting point for this study is that the generic approach has been accepted as the only logical procedure for developing regulations for fugitive emissions or for storage. Industry study reports have been issued that establish a basis for these regulations, based on the equipment, the operating conditions, and the physical properties of the chemicals involved. To generate generic process-emission standards, a procedure is developed that relates unit processes, unit operations, and physical properties consistent with the approach used for fugitive and storage emissions.

In this study the applicability of a generic regulatory approach to unit processes (reactions) and to unit operations is investigated. Priorities were determined by use of established survey and ranking data to identify the unit processes and unit operations associated with the greatest emissions. The survey and ranking program established that 140 compounds account for an estimated 86% of the SOCMI VOC emissions and identified the unit processes and unit operations associated with the production of each compound.

B. STANDARD SUPPORT

The generic standard methodology is comprised of three parts. The first part consists of projecting the emissions involved through establishing the VOC emission range to be expected and defining the method that will best estimate the ranges of total flow and VOC concentration for the particular process group being considered (i.e., air-oxidation processes, vacuum systems). Maximum and minimum flow and VOC concentrations are established. Therefore since all possible emissions from the concerned generic grouping are described, the most appropriate control method or methods can be identified. It is important to mention that the emission projection is not intended to be an exact predictive method for forecasting emission data. Although this would be desirable, it is sufficient for the emission projection to generate data for a reasonable range of flow and composition. This range then allows application of the control-device evaluation and costs to determine the corresponding range of cost and energy impacts that will cover the reasonable scope of emissions in SOCMI.

The second part of the generic standard methodology consists of an evaluation of applicable control devices. An assessment must be made of the applicability of the control device to the emission ranges concerned. The control-device design criteria must be established, and the emission variables having significant impact on control device design must be identified. This will lead to a set of specific designs, utilizing the proper design equations and procedures, that will adequately represent the application of the control device to the control of VOC emissions within the specified emission ranges. Control-device capital costs and operating costs are generated for various key flows and compositions. Control-device evaluation reports have been prepared for the EPA on thermal oxidizers, high-temperature thermal oxidizers, catalytic oxidizers, carbon adsorbers, absorbers, condensers, and flares and the use of emissions as fuel in which the technical and economic applicability of each control device to various organic emissions is assessed.

The third part of the methodology consists of an impact assessment. The cost and energy effectiveness must be determined for each control device evaluated over the appropriate range of flows and composition based on information from the emission projection and control device evaluation reports.

Knowledge of the emission range control technology and costs of control will lead to the development of an optimal standard for each generic area.

C. PROJECTION OF VOC EMISSIONS

1. Total Flow

To satisfy the first part of the generic standard support approach, methods must be defined to estimate the emissions total flow and VOC concentration range (thereby the total VOC flow) for the generic area being developed. In order to accomplish this, a common factor between most air emissions is sought. In this study it is assumed that an organic air emission can result from chemical process equipment if a gas is purged from the equipment into the atmosphere and if the gas contacts liquid or solid organics within the equipment. This gas is called the carrier gas, which is defined as an organic or inorganic compound that exists as a vapor or gas at the temperatures and pressures existing at the emission point. If a chemical process vessel does not generate a carrier gas, it cannot have an organic emission. (This analysis does not include air emissions arising from liquid- or solid-waste streams such as some fugitive or secondary emissions. In some fugitive emissions, leaking liquids or solids evaporate to generate an organic emission. In some secondary emissions, liquid or solid streams are exposed to the atmosphere and the organics evaporate, generating organic emissions.)

The assumption in the preceding paragraph allows chemical processes to be classified and ranked through an analysis of the possibility that each process will generate a carrier gas. Chemical reactions generate carrier gases because of the reactions themselves and because of mechanisms unrelated to the reaction.

a. Reaction-Related Carrier Gases——Chemical reactions generate carrier gases in several ways. The reactants for a specific reaction may contain gaseous impurities or may have an excess amount of a gaseous reactant for that particular reaction. A product or by-product from a reaction can also be a potential carrier gas.

In every case two additional conditions must be satisfied for a potential carrier gas to actually be emitted from the equipment: the potential carrier gases must not disappear as a result of reacting to nongaseous chemicals before being emitted and they must not have a net change in physical state from gases to liquids or become adsorbed on solids. In other words once gases are formed or introduced in the equipment, they must remain gases up to the point of discharge or be stripped or desorbed from any liquids or solids at the point of discharge. For example, carbon dioxide may be generated in an oxidation reaction but if it is scrubbed in a caustic scrubber, much of it can be converted to nongaseous inorganic carbonates and thus prevent an emission. Some organic compounds with normal boiling points greater than the ambient temperature may exist as gases inside the chemical equipment but are normally condensed before being emitted. These compounds are not carrier gases.

b. Nonreaction-Related Carrier Gases——Potential carrier gases are introduced into chemical process equipment for reasons unrelated to reactions; one reason is to control the physical conditions (temperature, pressure) in process equipment, another is to control the chemical atmosphere in process equipment, and the third one is uncontrolled leakage into equipment under reduced pressure.

Gases used to control physical conditions—Gases such as air, N_2, CO_2, and others are sometimes introduced into process equipment to cause cooling, heating, or elevated pressures or to control the pressure of vacuum systems. For processes operating under high pressure the amount of gases introduced can be significent. Slightly elevated pressures may be required for control of fluid flow or for transfer operations. Ultimately, gases used to achieve elevated pressures are released as potential carrier gases when the process streams return to atmospheric pressure at the end of the process train. This may be a continuous emission in continuous equipment or a periodic emission in batch or continuous equipment. Unexpected depressurization results in an upset emission.

Gases used to control the chemical atmosphere—Sometimes flammable or reactive chemicals are handled in chemical equipment, often requiring that the gaseous atmosphere in the equipment be controlled so as to prevent detonation, deflagration, or decomposition. Inert gases (gases that do not react under the conditions in the equipment being used) or organic gases are used to ensure that detonation, deflagration, or decomposition does not occur. Inert gases can also be used to sweep away gaseous reaction by-products that cause corrosion, decreased reaction rates, or other deleterious effects on the equipment performance.

Gases resulting from leakage because of reduced pressure—The two preceding cases (gases introduced to control conditions and the chemical atmosphere) are usually under some control by the plant designers or operating personnel. However, this case of leaks introducing gases into vessels under vacuum is largely beyond the control of plant personnel. This carrier gas results from air leaking into vacuum equipment through small seal imperfections and discontinuities caused by a pressure drop between the environment and the vacuum. Air that leaks into the equipment is normally emitted from the vacuum devices as a carrier gas.

c. Sources with Multiple Types of Carrier Gases—All chemical processes can be analyzed in terms of the gas sources mentioned above. Very few chemical processes generate carrier gases from only one mechanism. However, sometimes one mechanism from a source will override all the other mechanisms. Air-oxidation processes, for instance, generate carrier gases because of the inert nitrogen and unreacted oxygen introduced with the air, the carbon monoxide, and the carbon dioxide generated in the reaction. Some vapor-phase air oxidations also generate vapor-phase organic products that are potential carrier gases. With some air oxidations an inert gas is used for control of the reaction conditions or of the chemical atmosphere.

This one type of reaction, air oxidation, can generate carrier gases from a variety of mechanisms, but the overriding mechanism of emission formation is the inert nitrogen fed in the air as an impurity. Since the nitrogen is a function of the reaction stoichiometry, the range of carrier gas flow and ultimately the VOC emission can be projected. On the other hand in vacuum equipment the major carrier gas is largely generated by the leakage of air into the equipment although carrier gases can arise from the control of pressure, temperature, or chemical atmosphere or from reactions. Specific generic standard reports have been prepared that illustrate emission projection for both air-oxidation processes (a reaction-based approach) and vacuum systems (a nonreaction-based approach). These reports are contained in this volume.

Sometimes organic emissions arise when a process upset or runaway reaction causes a rapid buildup of carrier gas, which is released for safety reasons. These upset releases arise from the mechanisms mentioned above. Liquids that volatilize more rapidly than they can be condensed or stored in existing equipment can create an organic carrier gas from a chemical that is normally a liquid at atmospheric conditions. For example, a reactor with, say, liquid benzene could experience a rapid increase in temperature or decrease in pressure, causing the benzene to boil inside the equipment. This benzene vapor could become a carrier gas if insufficient cooling capacity existed before the emission was discharged. Benzene vapor could escape through equipment vents as a carrier gas and immediately dissipate in the atmosphere before it would be able to condense. A separate report on upset releases is included in this volume.

2. VOC Concentration

The concentration of VOC in the emission must be estimated in order to calculate the total amount of VOC emitted. It is difficult to generalize about this concentration. If the carrier gas flow is much larger than the VOC flow can possibly be, a maximum can be set on the VOC concentration. For example, air-oxidation processes generate so much carrier gas that even if the entire plant chemical production was VOC, the VOC concentration would be less than 5 mole %. In this special case VOC emissions are likely to be very large, whereas the VOC concentration will be very small. In other cases the chemicals being processed must be known in order for the VOC concentration to be calculated.

When the VOC normal boiling points are greater than the ambient temperature (organics that are liquids or solids at normal conditions) and the chemicals are known, the VOC content can be estimated by assuming saturation at the emission temperature. Although this will normally be a high estimate, it is sufficient to yield a VOC emission range and therefore enable control devices to be selected and cost estimates to be developed. If the normal boiling point of the VOC is less than the ambient temperature, then the VOC itself can be an organic carrier gas and can be the overriding VOC contributor for that emission. VOC for this case can be estimated from the techniques given in the report in this volume entitled Emission Projections for Carrier-Gas-Producing Reactions.

REPORT 2

EMISSION PROJECTIONS FOR CARRIER-GAS-PRODUCING REACTIONS

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I. THE GENERIC STANDARD APPROACH

For a discussion of the basis for the generic standard concept see Report 1 in this volume entitled The Generic Standard Approach. The reader is advised to read this report since the concept and essential terminology are explained therein.

II. CARRIER-GAS-GENERATING PROCESSES IN THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY

The synthetic organic chemicals industry is comprised of a wide variety of unit processes. Table II-1 gives the relative VOC emission ranking developed by IT Enviroscience for 140 different chemicals manufactured in the industry. This ranking is based on the total VOC emissions from storage, fugitive, secondary, and process emissions, as well as on an estimate of the severity of the VOC being emitted from the standpoint of quantity and toxicology. In addition the process emission can arise from all process operations-reactions, distillations, crystallizations, etc. This ranking was used to target 64 products and 97 processes that have been specifically addressed in 39 product reports prepared as part of this program. These reports cover over 85% of the VOC emissions initially projected for 1982. Further discussion of this ranking may be found in Appendix B of Volume 1.

Table II-1 also presents a ranked listing of products and the unit processes or reactions used to manufacture them. More than one process can be used to manufacture a product and more than one type of reaction can be used. For example, ethylene dichloride can be manufactured by either the oxychlorination or the direct chlorination process. In the production of methyl methacrylate a series of different reactions are used to convert the reactants to methyl methacrylate. The first reaction in a series for a particular product is designated "A" and the next "B." More than one "A" for a product indicates that the product is made by more than one unit process, but was not assigned additional processes. The unit processes (reactions) identified in the table are based on a rather specific classification of processes. For instance, oxyacetylation, oxychlorination, and ammoxidation are listed but are all special cases of oxidation. The specificity is required because the actual reaction chemistry and stoichiometry are often needed to develop emission projections.

Table II-2 is a compilation of the major unit processes and their total 1982 estimated production and emissions as developed in the ranking process mentioned above. Products that make up the unit processes are grouped and shown in Appendix A.

Table II-1. Unit Processes Used for the Manufacture of 140 Synthetic Organic Chemicals[a,b]

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammondysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrachlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
1. VINYL CHLORIDE	1% ACETYLENE																															A										
1. VINYL CHLORIDE	99% ETHYLENE DICHLORIDE												A																												
2. ACRYLONITRILE	100% PROPYLENE OXIDATION					A																																			
3. ETHYLENE DICHLORIDE	50% DIRECT CHLORINATION									A																															
3. ETHYLENE DICHLORIDE	50% OXYCHLORINATION																															A										
4. MALEIC ANHYDRIDE	85% BENZENE OXIDATION																												A													
4. MALEIC ANHYDRIDE	15% BUTANE OXIDATION																												A													
5. ETHYLENE OXIDE	66% AIR OXIDATION/ETHYLENE																												A													
5. ETHYLENE OXIDE	34% O2 OXIDATION/ETHYLENE																												A													
6. DIMETHYL TEREPHTHALATE (DMT)	23% AMOCO VIA TEREPHTHALIC ACID														B													A													
6. DIMETHYL TEREPHTHALATE (DMT)	35% DUPONT														B													A													
6. DIMETHYL TEREPHTHALATE (DMT)	17% EASTMAN VIA TEREPHTHALIC ACID														B													A													
6. DIMETHYL TEREPHTHALATE (DMT)	25% HERCULES														B													A													
7. ETHYLENE	46% NAPTHA GAS OIL PYROLYSIS																																		A							
7. ETHYLENE	52% NATURAL GAS LIQUIDS PYROLYSIS																																		A							
7. ETHYLENE	2% REFINERY BY-PRODUCT																																								A	
8. ETHYLBENZENE	98% BENZENE ALKYLATION			A																																						
8. ETHYLBENZENE	2% MIXED XYLENE EXTRACT																																								A	
9. HYDROGEN CYANIDE (HCN)	50% ACRYLONITRILE COPRODUCT					A																																			
9. HYDROGEN CYANIDE (HCN)	50% ANDRUSSOW PROCESS					A																																			
10. STYRENE	100% ETHYL BENZENE													A																												
11. 1,1,1, TRICHLOROETHANE	10% ETHANE CHLORINATION									A																															
11. 1,1,1, TRICHLOROETHANE	74% VINYL CHLORIDE									B									A																					
11. 1,1,1, TRICHLOROETHANE	16% VINYLIDENE CHLORIDE																			A																					
12. CARBON TETRACHLORIDE	38% CARBON DISULFIDE									A																															
12. CARBON TETRACHLORIDE	47% CHLOROPARAFFIN CHLORINOLYSIS									B																								A							
12. CARBON TETRACHLORIDE	20% METHANE									A																															
13. FORMALDEHYDE	23% METAL OXIDE/METHANOL																												A													
13. FORMALDEHYDE	77% SILVER CATALYST/METHANOL																												A													

Table II-1. (continued)

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
14. METHYL METHACRYLATE (MMA)	100% ACETONE CYANOHYDRIN															B										A																	
15. PROPYLENE OXIDE	60% CHLOROHYDRIN										A																												B				
15. PROPYLENE OXIDE	40% PEROXIDATION											B																						A									
16. PROPYLENE	54% NAPTHA/GAS OIL PYROLYSIS																																			A							
16. PROPYLENE	16% NATURAL GAS LIQUIDS PYROLYSIS																																			A							
16. PROPYLENE	30% REFINERY BY-PRODUCT																																									A	
17. NITROBENZENE	100% BENZENE NITRATION																												A														
18. ETHYLENE GLYCOL	100% ETHYLENE OXIDE																		A																								
19. CYCLOHEXANOL/CYCLOHEXANONE	75% CYCLOHEXANE																													A													
19. CYCLOHEXANOL/CYCLOHEXANONE	25% PHENOL																								A																		
20. CUMENE	100% BENZENE				A																																						
21. METHANOL (METHYL ALCOHOL)	100% METHANE																																			A	B						
22. PHENOL	3% CHLOROBENZENE	B																								A																	
22. PHENOL	2% BENZENE SULFONATION	B																C										B												A			
22. PHENOL	93% CUMENE																													A													
22. PHENOL	2% TOLUENE OXIDATION																													A													
23. ANILINE	100% NITROBENZENE HYDROGENATION																								A																		
24. FLUOROCARBONS	100% CCL4/C2CL6 FLUORINATION																A																										
25. PERCHLOROETHYLENE	66% ETHYLENE DICHLORIDE										A																																
25. PERCHLOROETHYLENE	34% ETHANE CHLORINOLYSIS										B																									A							
26. TEREPHTHALIC ACID (TPA)	39% AMOCO																													A													
26. TEREPHTHALIC ACID (TPA)	47% EASTMAN																													A													
26. TEREPHTHALIC ACID (TPA)	14% MOBIL																													A													
27. CHLOROBENZENE	100% BENZENE CHLORINATION										A																																
28. ACRYLIC ACID	23% MODIFIED REPPE								A																																		
28. ACRYLIC ACID	77% PROPYLENE OXIDATION																													A													
29. ACETIC ACID	33% ACETALDEHYDE																													A													
29. ACETIC ACID	44% BUTANE OXIDATION																													A													
29. ACETIC ACID	19% METHANOL								A																																		
29. ACETIC ACID	4% OTHERS																																										

Table II-1. (continued)

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
30. CHLOROPRENE	100% VIA BUTADIENE										A			C													B																
31. ALKYL LEADS	5% ELECTROLYSIS																																					A					
31. ALKYL LEADS	95% ETHYL CHLORIDE				A																																						
32. ACETONE	69% CUMENE																													A													
32. ACETONE	31% ISOPROPANOL														A															A													
33. ETHYL CHLORIDE	4% ETHANOL/ETHANE										A																																
33. ETHYL CHLORIDE	96% ETHYLENE CHLORINATION																				A																						
34. ETHANOLAMINES	100% ETHYLENE OXIDE					A																																					
35. VINYL ACETATE (VA)	13% ACETYLENE VAPOR PHASE		A																																								
35. VINYL ACETATE (VA)	72% ETHYLENE VAPOR PHASE																															A											
35. VINYL ACETATE (VA)	15% ETHYLENE LIQUID PHASE																															A											
36. METHYLENE CHLORIDE	35% METHANE CHLORINATION										A																																
36. METHYLENE CHLORIDE	65% METHANOL/METHYL CHLORIDE										A																																
37. 1,3 BUTADIENE	80% ETHYLENE COPRODUCT																																			A							
37. 1,3 BUTADIENE	13% N-BUTANE																																			A							
37. 1,3 BUTADIENE	7% N-BUTENE																																			A							
38. VINYLIDENE CHLORIDE	50% 1,1,1 TRICHLOROETHYLENE													A																													
38. VINYLIDENE CHLORIDE	50% 1,1,2 TRICHLOROETHYLENE													A																													
39. TOLUENE DIISOCYANATE (TDI)	100% DIAMINOTOLUENE																																		A								
40. CHLOROFORM	63% METHANE CHLORINATION										A																																
40. CHLOROFORM	37% METHANOL CHLORINATION										A																																
41. PHTHALIC ANHYDRIDE	30% NAPTHALENE																													A													
41. PHTHALIC ANHYDRIDE	70% O-XYLENE																													A													
42. ISOPROPANOL (ISOPROPYL ALCOHOL)	100% PROPYLENE/SULFURIC ACID																		B																					A			
43. ACETIC ANHYDRIDE	100% ACETIC ACID																													A													
44. GLYCEROL (SYNTHETIC ONLY)	14% ACROLEIN																		C						A									B									
44. GLYCEROL (SYNTHETIC ONLY)	15% ALLYL ALCOHOL																		B															A									
44. GLYCEROL (SYNTHETIC ONLY)	71% EPICHLOROHYDRIN										A			B					C																								
45. NITROPHENOL	100% PHENOL NITRATION																												A														

Table II-1. (continued)

roduct	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
46. CYCLOHEXANE	84% BENZENE HYDROGENATION																								A																		
46. CYCLOHEXANE	16% PETROLEUM DISTILLATION																																									A	
47. BISPHENOL A	100% PHENOL/ACETONE											A																															
48. CELLULOSE ACETATE	100% CELLULOSE ESTERIFICATION															A																											
49. CAPROLACTAM	100% CYCLOHEXANONE																										B	C			A												
50. PENTAERYTHRITOL	100% FORMALDEHYDE/ACETALDEHYDE											A																															
51. NONYL PHENOL	100% PHENOL ALKYLATION				A																																						
52. ACRYLAMIDE	100% ACRYLONITRILE																									A																	
53. DIETHYLENE, TRIETHYLENE GLYCOLS	100% COPRODUCTS W/ETHYLENE GLYCOL																		A																								
54. FUMARIC ACID	100% MALEIC ACID/ISOMERIZATION																										A																
55. PROPYLENE GLYCOLS (MONO,DI,TRI)	100% PROPYLENE OXIDE HYDRATION																		A																								
56. EPICHLOROHYDRIN	100% ALLYL CHLORIDE/HCL																									A																	
57. ALLYL CHLORIDE	100% PROPYLENE CHLORINATION										A																																
58. ADIPONITRILE/HMDA	11% ACRYLONITRILE																						A																				
58. ADIPONITRILE/HMDA	24% ADIPIC ACID					A																																					
58. ADIPONITRILE/HMDA	65% BUTADIENE																			A					B																		
59. TRICHLOROETHYLENE	9% ACETYLENE										A																																
59. TRICHLOROETHYLENE	91% ETHYLENE DICHLORIDE																				A													A									
60. METHYL ISOBUTYL KETONE (MIBK)	100% ACETONE											B		C											A																		
61. PYRIDINE	100% FORMALDEHYDE/ACETALDEHYDE					A																																					
62. BENZENE	80% NOT IN PROJECT SCOPE																																									A	
62. BENZENE	20% TOLUENE HYDRODEALKYLATION																					A																					
63. ETHANOL (ETHYL ALCOHOL)	100% ETHYLENE																		A						B																		
64. UREA	100% AMMONIA/CARBON DIOXIDE											A	B																														
65. ACETALDEHYDE	100% ETHYLENE																													A													
66. ISOPRENE	67% C4 HYDROCARBONS																																									A	
66. ISOPRENE	33% ISOAMYLENE EXTRACTION														A																												
67. FURFURAL	100% POLYSACCHARIDES HYDROLYSIS																									A																	
68. GLYCOL ETHERS	97% ETHYLENE OXIDE			A																																							
68. GLYCOL ETHERS	3% PROPYLENE OXIDE			A																																							

Table II-1. (continued)

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
69. DINITROTOLUENE	100% TOLUENE DINITRATION																												A														
70. SEC-BUTANOL	100% BUTYLENES																		B																				A			
71. LINEAR ALKYL BENZENE	100% BENZENE ALKYLATION				A																																						
72. ACROLEIN	100% PROPYLENE OXIDATION																													A													
73. DIPHENYLAMINE	100% ANILINE AMINATION											A																															
74. METHYL STYRENE	15% CUMENE DEHYDROGENATION														A																												
74. METHYL STYRENE	85% CUMENE PROCESS BY-PRODUCT				A																																						
75. ETHYLENE DIAMINE/TRIETHYLENE TETRAMINE	100% EDC AMMONOLYSIS					A																																					
76. ETHYL ACRYLATE	61% ACETYLENE (REPPE)								A																																		
76. ETHYL ACRYLATE	37% DIRECT ESTERIFICATION															A																											
77. METHYL CHLORIDE	2% METHANE CHLORINATION										A																																
77. METHYL CHLORIDE	98% METHANOL HYDROCHLORINATION																				A																						
78. METHYLENE DIPHENYLENE DIISOCYANATE	100% DPMDA/PHOSGENE																																		A								
79. N-BUTYRALDEHYDE	100% OXO PROCESS																					A																					
80. NITROANILINE	100% NITRO CHLOROBENZENE																												A														
81. ACETOPHENONE	60% CUMENE PEROXIDATION																																	A									
81. ACETOPHENONE	40% ETHYL BENZENE OXIDATION																													A													
82. ISOPHTHALIC ACID	100% M-XYLENE OXIDATION																													A													
83. BENZOIC ACID	100% TOLUENE AIR OXIDATION																													A													
84. DIISOOCTYL PHTHALATE (DI2-ETHYLHEXYL)	100% PHTHALIC ANHYDRIDE/ALCOHOL															A																											
85. 2-ETHYL 1-HEXANOL	100% CONDENSATION											A	D												C																		
86. N-BUTANOL (BUTYL ALCOHOL)	20% ACETALDEHYDE											A													B																		
86. N-BUTANOL (BUTYL ALCOHOL)	80% OXO PROCESS																							A																			
87. PROPIONIC ACID	7% OTHERS																																										
87. PROPIONIC ACID	93% OXO PROCESS																							A																			
88. ETHYL ACETATE	100% ACETIC ACID															A																											
89. ETHYLENE DIBROMIDE	100% ETHYLENE BROMINATION							A																																			
90. ACETONE CYANOHYDRIN	100% ACETONE CYANATION																			A																							
91. BENZYL CHLORIDE	100% TOLUENE CHLORINATION										A																																

Table II-1. (continued)

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation	Separation
92. DICHLOROPHENOL	45% PHENOL CHLORINATION										A																														
92. DICHLOROPHENOL	55% TRICHLOROBENZENE													A																											
93. ISOBUTYRALDEHYDE	100% OXO PROCESS																							A																	
94. CRESYLIC ACIDS (SYN)	4% CYMENE OXIDATION																													A											
94. CRESYLIC ACIDS (SYN)	80% NATURAL COAL TAR																																								A
94. CRESYLIC ACIDS (SYN)	8% PHENOL/METHANOL				A																																				
94. CRESYLIC ACIDS (SYN)	8% TOLUENE SULFONATION																	B																						A	
95. N-N DIMETHYL ANILINE	100% ANILINE ALCOHOLYSIS			A																																					
96. ACETYLENE	30% CALCIUM CARBIDE																		A																						
96. ACETYLENE	8% ETHYLENE BY-PRODUCT																																								A
96. ACETYLENE	62% HYDROCARBON OXIDATION																													A											
97. PHOSGENE	100% CARBON MONOXIDE/CHLORINE										A																														
98. T-BUTANOL	21% ISOBUTYLENE																											B													A
98. T-BUTANOL	79% PROPYLENE OXIDE CO-PRODUCT										A																												B		
99. SALICYLIC ACID	100% SODIUM PHENATE	B							A																																
100. DIMETHYL HYDRAZINE	100% NITROSODIMETHYL AMINE																													A											
101. DODECENE	100% NONENE CO-PRODUCT																																								A
102. DIISODECYL PHTHALATE	100% PHTHALIC ANHYDRIDE/ISODECANOL															A																									
103. BUTYL ACRYLATE	100% ACRYLIC ACID ESTERIFICATION															A																									
104. CHLOROSULFONIC ACID	100% SO3 HYDROCHLORINATION																				B																			A	
105. METHYL ETHYL KETONE (MEK)	25% BUTANE OXIDATION																													A											
105. METHYL ETHYL KETONE (MEK)	75% SEC-BUTANOL														A																										
106. ISOBUTANOL (ISOBUTYL ALCOHOL)	100% OXO PROCESS																							A																	
107. HYDROQUINONE	100% ACETONE CO-PRODUCT									B																				A											
108. MONO-DI-TRI-METHYL AMINES	100% METHANOL AMMONOLYSIS					A																																			
109. ADIPIC ACID	100% CYCLOHEXANE																													A											
110. CHLORONITROBENZENE	100% CHLOROBENZENE NITRATION																												A												
111. CARBON DISULFIDE	100% METHANE/SULFUR VAPOR																													A											
112. BIPHENYL	100% TOLUENE HYDRODEALKYLATION																					A																			
113. ACETYL CHLORIDE	100% SODIUM ACETATE										A																														

Table II-1. (continued)

Product	Process	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammonolysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrochlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
114. MONO,DI,TRI,ETHYL AMINE	100% ETHANOL AMMONOLYSIS					A																																						
115. CHLOROACETIC ACID	100% ACETIC ACID CHLORINATION										A																															
116. BENZOPHENONE	100% BENZENE/CARBON TETRACHLORIDE				A																					B																	
117. METHYL BROMIDE	100% METHANOL/HBR AND BROMINE							A																																		
118. PROPYL ALCOHOL	87% OXO PROCESS																							A																			
118. PROPYL ALCOHOL	13% PROPANE OXIDATION																													A													
119. BUTYL AMINES	100% BUTYRALDEHYDE HYDROGENATION					B														A					A																		
120. ETHYL (DIETHYL) ETHER	100% ETHANOL												A																													
121. PROPYL AMINES (M-D-T)	50% N-PROPYL ALCOHOL					A														A																							
121. PROPYL AMINES (M-D-T)	50% N-PROPYL CHLORIDE					A																																				
122. CROTONALDEHYDE	100% ALDO PROCESS												B																										A				
123. ISOOCTYL ALCOHOL	100% OXO PROCESS/HYDROGENATION																							A																			
124. FORMIC ACID	90% N-BUTANE OXIDATION																													A													
125. ETHYLENE GLYCOL METHYL ETHYL ETHER ACETATE	100% ETHOXY ETHANOL ESTER															A																										
126. LINEAR ALKYL BENZENE SULFONATE	100% LAB SULFONATION																																							A			
127. ISODECANOL	25% N-PARAFFIN OXIDATION																													A													
127. ISODECANOL	75% OXO PROCESS																							A																			
128. ALLYL ALCOHOL	47% ALLYL CHLORIDE HYDROLYSIS																									A																	
128. ALLYL ALCOHOL	6% PROP GLYCOL DEHYDRATION												A																													
128. ALLYL ALCOHOL	47% PROP OXIDE ISOMERIZATION																										A																
129. ISOPROPYL ACETATE	100% ISOPROPANOL ESTERIFICATION															A																										
130. METHYL ACETATE	100% ACETIC ACID/METHANOL															A																										
131. CYCLOOCTADIENE	100% BUTADIENE DIMERIZATION											A																														
132. HEXACHLOROBENZENE	100% HEXACHLOROCYCLOHEXANE										A				B																												
133. N-BUTYL ACETATE	100% ESTERIFICATION															A																										
134. BUTYRIC ACID	33% BUTYRALDEHYDE OXIDATION																													A													
134. BUTYRIC ACID	67% N-BUTANE OXIDATION																													A													
135. DINITROPHENOL	100% DINITRATION OF PHENOL																									A																	
136. AMINO ETHYLETHANOLAMINE	100% ETHYLENE OXIDE					A																																				

Table II-1. (continued)

Product[c]	Process[d]	Acidification	Addition Esterification	Alcoholysis	Alkylation	Ammondysis	Ammoxidation	Bromination	Carbonylation	Cleaving	Chlorination	Condensation	Dehydration	Dehydrachlorination	Dehydrogenation	Esterification	Fluorination	Fusion	Hydration	Hydrocyanation	Hydrochlorination	Hydrodealkylation	Hydrodimerization	Hydroformylation	Hydrogenation	Hydrolysis	Isomerization	Neutralization	Nitration	Oxidation	Oximation	Oxyacetylation	Oxychlorination	Peroxidation	Phosgenation	Pyrolysis	Reforming	Reduction	Saponification	Sulfonation		Separation	
137. CYCLOHEXYLAMINE	50% ANILINE																								A																		
137. CYCLOHEXYLAMINE	50% CYCLOHEXANONE					A																																					
138. TOLUENE SULFONIC ACIDS	100% TOLUENE SULFONATION																																							A			
139. BENZYL BENZOATE	50% BENZALDEHYDE															B														A								A					
139. BENZYL BENZOATE	50% BENZYL ALCOHOL/ACID															A																											
140. BENZOYL CHLORIDE	100% BENZOIC ACID										A																																

[a] Based on an IT Enviroscience survey and ranking study.

[b] First reaction in a series is designated "A", the second "B", etc. More than one A for a product indicates that the product is made by more than one unit process, but was not assigned additional processes.

[c] Ranking numbers are from the IT Enviroscience Survey and Ranking Study and are based upon total estimated 1982 emissions for that process and the toxicity of the emission.

[d] Percentages indicate the percentage of 1982 estimated production for that product made by that process.

Table II-2. Estimated Total VOC Emissions from Process, Fugitive, and Storage and Secondary Sources for Major Unit Processes Based on Early ITE Ranking Studies

Unit Process	1982 Estimated Production (M̄* lb/yr)	1982 Estimated Total VOC Emissions (M̄ lb/yr)
Oxidation	37,300	528
Ammoxidation	3,420	301
Esterification	7,700	182
Chlorination	16,100	175
Pyrolysis (chlorinolysis)	56,100	173
Dehydrochlorination	9,500	91
Oxychlorination	6,030	72
Alkylation	14,400	59
Hydrolysis	1,900	56
Hydration	10,800	52
Saponification	2,960	50
Reforming	9,370	39
Hydrogenation	7,210	31
Hydrochlorination	2,020	22
Condensation	14,300	20
Isomerization	1,590	19
Oxyacetylation	1,930	17
Dehydrogenation	10,900	13
Hydrocyanation	1,670	12
Dehydration	12,200	10
Sulfonation	3,710	9
Nitration	2,380	8
Carbonylation	1,080	7
Phosgenation	1,630	7
Hydrofluorination	1,000	5
Oximation	1,080	5
Neutralization	1,480	5
Hydroformylation	1,620	4
Ammonolysis	1,380	4
Peroxidation	1,360	3

Table II-2. (Continued)

Unit Process	1982 Estimated Production ($\bar{M}$ lb/yr)	1982 Estimated Total VOC Emissions ($\bar{M}$ lb/yr)
Hydrodealkylation	4,030	3
Addition esterification	290	2
Bromination	220	1
Alcoholysis	1,110	<1
Cleaving	25	<1
Acidification	220	<1
Fusion	84	<1
Reduction	45	<1

*Designates one million.

The data presented in Tables II-1 and II-2 are based on the total emissions from the 140 products surveyed by IT Enviroscience. These data, however, do not indicate the relative importance of the emissions from one reaction over that from another reaction. Data from nearly 200 trip reports and letter responses to EPA requests for information, given in Appendix B, were generated through the IT Enviroscience study and led to a data base of chemical reaction emissions. These data have been analyzed and organized to show the most significant reactions from a VOC-emission standpoint from the available data (no new data were collected specifically for this report because of time and budget constraints). Figure II-1 is a summary of the organic emissions from reactions on which real data are available. The emissions are based on the pounds of VOC emitted per million pounds of product produced; this ratio is based on the emissions actually entering the atmosphere as reported by industry and therefore represents a mixture of uncontrolled and controlled emissions for the unit processes from data collected from 1975—1979. These data sources are given in Appendix B. Unit processes designated with an asterisk indicate that less than four items of emission data were available. The dots designate the average values for all the data available, with the maximum and minimum values also shown. As would be expected, the ranges of emissions vary greatly because of the difference in the processes and because both controlled and uncontrolled plants exist in nearly every category.

A crude estimate of the emissions arising from reactors in each unit process can be made by multiplying the median value as shown in Fig. II-1 and by the total production of chemicals using that unit process, and is given in Table II-3.

Air-oxidation processes are clearly the leading emitters based on both the annual production and the estimated VOC emission ratio. A report specifically pertaining to air oxidation processes has been prepared.

The chlorination process, which is widely used throughout the industry, is the second highest emitter source (this catagory includes chlorohydrination). The chlorination reactions are analyzed later in this report.

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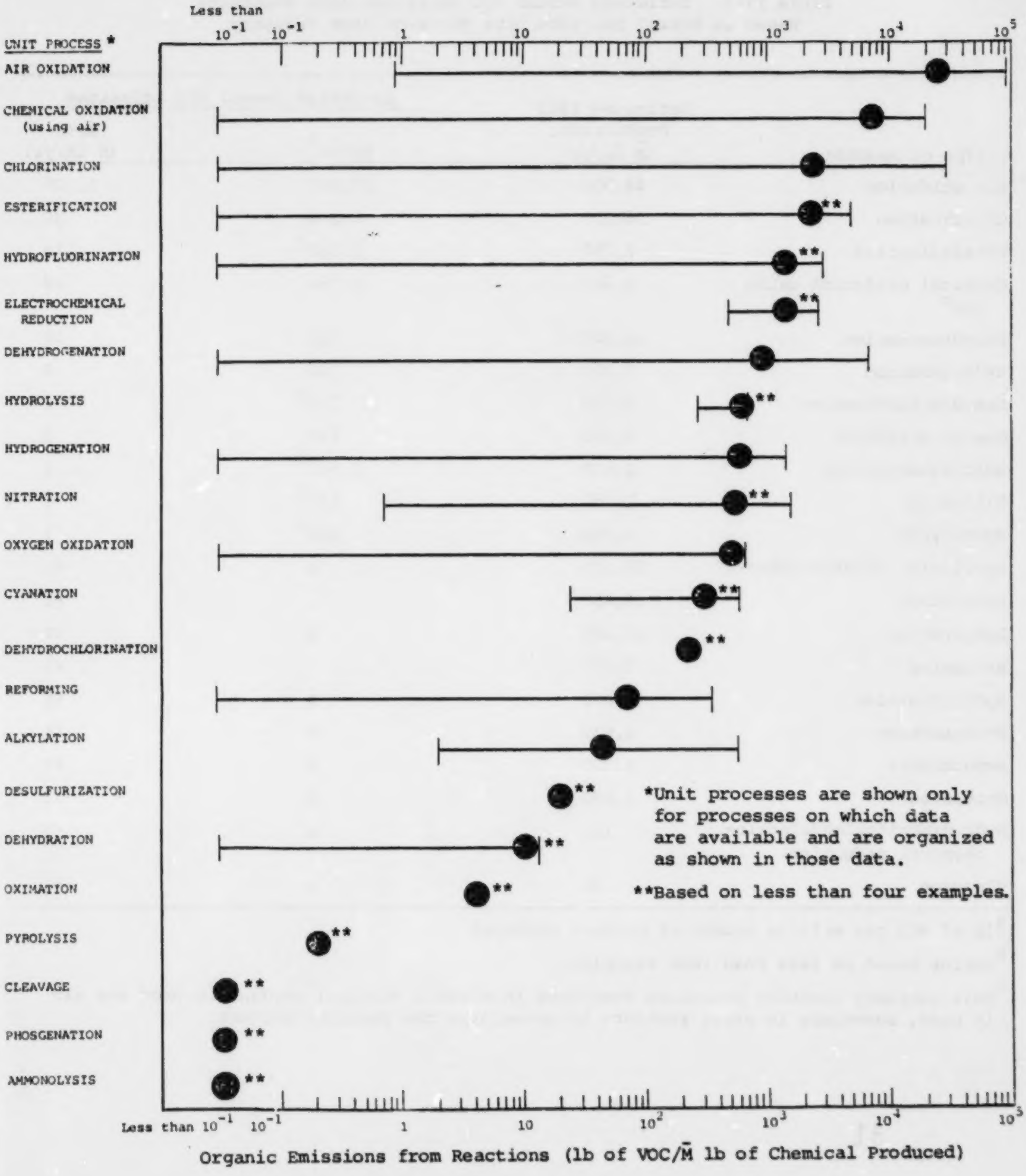

Fig. II-1. Actual VOC Reaction Emission Data

Table II-3. Estimated Annual VOC Emissions from Reactions Based on Actual Emission Data Received from Industry

Type of Reactor	Estimated 1982 Production ($\bar{M}$ lb/yr)	Estimated Annual VOC Emissions	
		Ratio[a]	Rate ($\bar{M}$ lb/yr)
Air oxidation	44,900	24,800	1,100
Chlorination	16,100	2,360	38
Esterification	7,700	2,300[b]	18
Chemical oxidation using air[c]	1,850	7,760	14
Dehydrogenation	10,900	910	10
Hydrogenation	7,210	580	4
Dehydrochlorination	9,500	230[b]	2
Oxygen oxidation	3,950	510	2
Hydrofluorination	1,000	1,540[b]	2
Nitration	2,380	530[b]	1
Hydrolysis	1,900	610[b]	1
Pyrolysis (chlorinolysis)	56,100	b	<1
Alkylation	14,400		<1
Dehydration	12,200	b	<1
Reforming	9,370		<1
Hydrocyanation	1,670	b	<1
Phosgenation	1,630	b	<1
Ammonolysis	1,380	b	<1
Oximation	1,080	b	<1
Hydrodimerization/electrochemical reduction	126	b	<1
Cleavage	25	b	<1

[a] lb of VOC per million pounds of product produced.

[b] Ratios based on less than four examples.

[c] This category includes oxidation reactions in which a chemical oxidant is used and air is used, sometimes in other reactors to re-oxidize the chemical oxidant.

The esterification processes, the third highest source of emissions (see Table II-3), typically have no reaction-related carrier gases associated with them. The emission ratio is based on only three items of data and may reflect the fact that inert carrier gases have been used in the reactor to prevent decomposition or operations in the explosion range. Further specific data are required on esterification processes to confirm the emission ratio in this widely used reaction.

Chemical oxidations using air are also significant emitters. This category is also covered in the Air Oxidation Emission Projection report in this volume.

Dehydrogenation has a relatively low emission ratio but has significant VOC emissions because of the large amount of products annually produced. In 1982 styrene production will account for 87% of the chemicals produced by dehydrogenation.

Hydrogenation is estimated to account for 4 million lb of VOC emitted per year. Most hydrogenation emissions are now burned as fuel or are controlled with a flare. The moderate emission ratio is caused by two factors: producers of hexamethylenediamine and caprolactam have low levels of VOC control, and flares and fuel burners are assumed to have a VOC destruction efficiency of 99% (emitting 1% of the VOC).

Dehydrochlorination reactions emit an estimated 2 million lb of VOC per year. However, only one item of data was available on this type of reactor and it relates to a product responsible for only 3% of 1982 production. Nearly 90% of the chemicals produced by dehydrochlorination reactors are from vinyl chloride manufacture. Regulations for this chemical have already been promulgated.

Oxygen oxidations, which are primarily used to make vinyl acetate and ethylene oxide, are also estimated to be significant emitters. All the actual data on these plants obtained by trip reports and EPA information requests indicate that the uncontrolled emissions are being sent to flares or are being used for fuel. The emission ratio estimated is therefore primarily based on 99% VOC destruction efficiency in the combustion control devices. It is felt that the bulk of these plants may already be controlled.

Hydrofluorination (sometimes referred to as fluorination) is used exclusively in the manufacture of fluorocarbons. Emissions from this category could be reduced through the requirement of higher levels of control. However, as stated in the product report on fluorocarbons, the bulk of the emissions in this industry results from distillation operations. Generic standards under development for distillations may require control devices to which the reactor emissions may also be routed.

The emissions ratio from nitration reactions is based upon only three data points. One has a large VOC emission with a relatively low level of control, whereas the other two have nearly negligible emission ratios. Further real data on nitration reactions should be collected before a generic standard for it is undertaken.

The hydrolysis reaction emission factor is based on two items of data. It is likely that these data overstate the estimated emission ratio and that the annual VOC emissions from hydrolysis reactions are less than 1 million lb/yr.

All the remaining reactions are projected to result in VOC emissions of less than 1 million lb/yr. However, these projections are often based on limited real data, and it is possible that plants in these groups exist that emit significant quantities of VOC. A different method is needed to estimate the potential magnitude of VOC emissions from processes on which there is limited information. In the next two sections a method is discussed that can be used in subsequent EPA projects to estimate other chemical reactions with potentially severe VOC emissions. Time and budget constraints prohibit the application of this method in this report. The method will be demonstrated with chlorination reactions used as an example.

III. EMISSIONS

A. INTRODUCTION

The next two chapters present a technique for estimating the likely range of organic emissions being generated by chemical reactions; the technique is based on the propensity for a given reaction to generate or use carrier gases. These carrier gases can be organic or inorganic gases and can arise from the reactants or products of the reaction or from nonreaction-related sources. In chapter IV, chlorination reactions are discussed as an example of this approach.

B. CARRIER GASES——ESTIMATION OF TOTAL FLOW

Carrier gases an be organized in two ways: according to their chemical class or by the method in which they are generated. The next two subsections deal with carrier-gas classification by chemical class. The subsections following the classification by chemical class deal with carrier-gas classification by functional source, that is, reaction-related and nonreaction-related carrier gases.

1. Inorganic Carrier Gases

Carrier gases are chemical compounds that exist as a gas at the temperature and pressure existing at the emission point. Inorganic gases are nearly always carrier gases, because their normal boiling points are significantly less than the temperatures at the emission point. Table III-1[1]* gives some examples of these various classes of inorganic carrier gases. Inorganic carrier gases can be nonreactive or inert, prone to conversion by oxidation, prone to conversion by reduction, or easily converted to a water-soluble ionized or salt form. Totally nonreactive gases are the noble gases in the Periodic Table and nitrogen. Other common gases (CO_2) are said to be inert in the sense that they do not react with oxygen or other organics, but from a carrier-gas viewpoint they can be converted by salt formation (carbonates) or other reactions. Gases prone to thermal or chemical oxidation can be converted to other gases (carbon monoxide to carbon dioxide) or to nongaseous compounds (hydrogen to steam and then condensed). This group can often be considered as candidates for combustion control or energy recovery as fuel if the combustion or control device can remove or recover nitrogen oxides or sulfur compounds from the flue gas.

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*See Sect. VI for references cited in this report.

Table III-1. Classification of Inorganic Carrier Gases

Classification	Some Inorganic Carrier Gases	Characteristics
Nonreactive	Nitrogen Argon Helium	Inert; will not undergo chemical reaction or conversion
Prone to conversion by oxidation	Hydrogen Carbon monoxide Sulfur dioxide Hydrogen sulfide Some NO_x	Can be thermally or chemically oxidized, forming another carrier gas or a nongaseous compound
Prone to conversion by reduction	Oxygen Ozone Chlorine Bromine Some NO_x	Can be thermally or chemically reduced, forming another carrier gas or a nongaseous compound
High water solubility or forms salts	Carbon dioxide Sulfur dioxide Sulfur trioxide Hydrogen chloride Hydrogen bromide Hydrogen fluoride Ammonia Some NO_x	Easily ionizes in water or converts to form salt with a high water solubility

Inorganic carrier gases that are prone to conversion by chemical reduction can be chemically or thermally reduced into nongaseous compounds. Chlorine can be removed by reacting it with a reducing agent such as a sodium bisulfite solution. Compounds that have a high water solubility (usually because they are easily ionized) or form soluble salts at certain pHs can be converted to nongaseous compounds in an acid, base, or neutral-pH water absorber. This classification allows identification of the chemical processes most likely to form and emit a carrier gas. Processes into which nitrogen, argon, or helium is fed or generated will likely lead to a carrier-gas emission (therefore a VOC) since these compounds are not converted to nongaseous compounds. Other inorganic gases may be emitted as carrier gases only if they are not converted by oxidation, reduction, or salt reactions to nongaseous compounds.

2. Organic Carrier Gases

Organic compounds can also be carrier gases if they exist as gases at the conditions of the emission. It is obvious that some organics are gases at ambient conditions (e.g., methane, ethane) but most organic compounds are liquids or solids at these conditions. Ambient conditions selected for this analysis are atmospheric pressure and temperatures that range from 16 to 32°C. Compounds that have a boiling point of less than, say, 32°C at atmospheric pressure are potential carrier gases. Compounds that have a normal boiling point in excess of 32°C usually cannot be carrier gases although they can exist as an organic component in another carrier-gas emission. Figure III-1 shows the normal boiling points for many classes of organic compounds as a function of the number of carbon atoms in each molecule. The curves shown in Fig. III-1 are based on homologs of one compound in each series. For instance, the alkane series show the boiling points of methane (1 carbon atom), ethane (2 carbon atoms), propane (3 carbon atoms), n-butane (4 carbon atoms), n-pentane (5 carbon atoms), and so on. Isomers of butane and pentane are not included. The curves therefore represent a typical but not comprehensive presentation of the boiling points of members of the different organic classes.

For the organic classes studied it becomes apparent that alkenes with 5 carbon atoms and less can be carrier gases; alkanes and alkynes with 4 carbon atoms and less can be carrier gases; ethers, chlorinated hydrocarbons, epoxides, amines and aldehydes and esters with 2 carbon atoms and less can be carrier

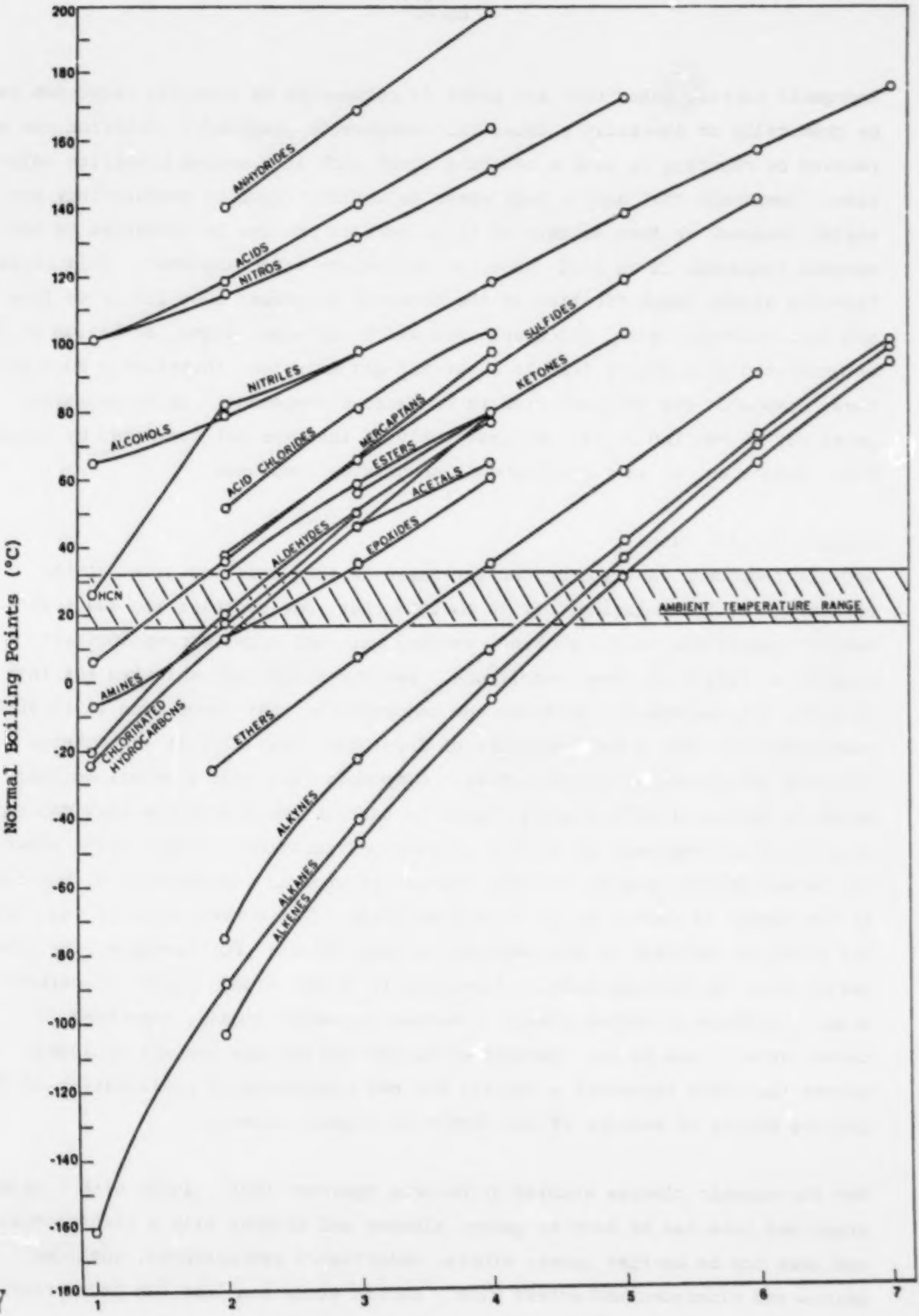

Fig. III-1. Organic Compound Normal Boiling Points

Table III-2. Organic Compounds Likely To Be Carrier Gases

Chemical Class	Compounds with Indicated Number of Carbon Atoms in Each Molecule				
	One	Two	Three	Four	Five
Alkenes and dienes		Ethylene	Propylene	Butylene, butadiene, and isomers	Pentene and isomers
Alkanes	Methane	Ethane	Propane	Butane and isomers	
Alkynes		Acetylene	Propyne	Butyne and isomers	
Ethers		Dimethyl ether	Methylethyl ether		
Chlorinated hydrocarbons	Methyl chloride[a,b]	Ethyl chloride[a,b] vinyl chloride			
Brominated hydrocarbons	Methyl bromide[a,b]				
Fluorinated hydrocarbons	Trichlorofluoromethane, dichlorodifluoromethane, chlorodifluoromethane	Dichlorotetrafluoroethane			
Epoxides		Ethylene oxide[a]			
Amines	Methyl amine[a]	Ethyl amine[a]			
Aldehydes	Formaldehyde[a]	Acetaldehyde[a]			
Esters		Methyl formate[a]			
Mercaptans	Methyl mercaptan[a]				
Nitriles	Hydrogen cyanide[a]				

[a] Can be removed or partly removed by water absorption at the appropriate pH.

[b] Secondary emissions from the absorber liquid effluent are likely.

gases; and mercaptans and nitriles with 1 carbon atom can be carrier gases. Organic compounds that cannot be carrier gases are acetals, ketones, sulfides, acid chlorides, alcohols, nitriles (except HCN), nitro-compounds, carboxylic acids, and acid anhydrides. Since the compounds that can be carrier gases are few in number and most often have the fewest numbers of carbon atoms in the series, a listing of many of the actual compounds can be presented. Table III-2 gives the specific organic compounds likely to be carrier gases.

All organic carrier gases are prone to oxidation and therefore may be candidates for burning for fuel or control. Many of the potential organic carrier gases have significant water solubilities and therefore can be physically removed by water absorption. Compounds that can be removed or controlled by water absorption are designated in Table III-2. Compounds that cannot be removed by water absorption can often be removed by an oil or hydrocarbon absorption process. Condensation may be possible if refrigerated condensers are used.

3. Reaction-Related Carrier Gases

Reaction-related carrier gases can arise from gaseous impurities in the reactants, excess gaseous reactants, and unrecovered gaseous products or by-products. The reaction-related carrier-gas flows can be estimated if the reaction stoichiometry, reactant purities, and amount of excess reactants are known or can be estimated.

The 140 products ranked for VOC emission potential (further discussed in Appendix B of Volume 1) have been studied and catagorized so as to identify the existence of inorganic and organic reaction-related carrier gases. Tables III-3 and III-4 represent a compilation of these data. Carrier gases that originate because of reactants are listed in Table III-3 and carrier gases that originate because of reaction products or by-products are given in Table III-4. Organic gases are denoted by type and carbon number, whereas inorganic gases are designated as to whether they are always or sometimes used or produced.

Products that are given in Tables III-3 and III-4 were organized to indicate which each group uses or produces a certain class of carrier gases, as shown in Appendix C. For instance all products that use or produce alkenes can be

Table III-3. Reaction-Reactant-Related Carrier Gases for 140 Synthetic Organic Chemicals

Product	Process	Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
1. VINYL CHLORIDE	1% ACETYLENE			CD			S							A								
1. VINYL CHLORIDE	99% ETHYLENE DICHLORIDE																					
2. ACRYLONITRILE	100% PROPYLENE OXIDATION			DC			A						A								A	
3. ETHYLENE DICHLORIDE	50% DIRECT CHLORINATION		PC											A								
3. ETHYLENE DICHLORIDE	50% OXYCHLORINATION		DC				S							A								
4. MALEIC ANHYDRIDE	85% BENZENE OXIDATION						A						A									
4. MALEIC ANHYDRIDE	15% BUTANE OXIDATION				DC		A						A									
5. ETHYLENE OXIDE	44% AIR OXIDATION/ETHYLENE		DC				A						A									
5. ETHYLENE OXIDE	34% O2 OXIDATION/ETHYLENE		DC					A					A									
6. DIMETHYL TEREPHTHALATE (DMT)	23% AMOCO VIA TEREPHTHALIC ACID						A						A									
6. DIMETHYL TEREPHTHALATE (DMT)	35% DUPONT						A						A									
6. DIMETHYL TEREPHTHALATE (DMT)	17% EASTMAN VIA TEREPHTHALIC ACID						A						A									
6. DIMETHYL TEREPHTHALATE (DMT)	25% HERCULES						A						A									
7. ETHYLENE	46% NAPTHA GAS OIL PYROLYSIS	A	DC	DC	DC	C																
7. ETHYLENE	52% NATURAL GAS LIQUIDS PYROLYSIS	A	DC	DC	DC	C																
7. ETHYLENE	2% REFINERY BY-PRODUCT	A	DC	DC	DC	C																
8. ETHYLBENZENE	98% BENZENE ALKYLATION		F																			
8. ETHYLBENZENE	2% MIXED XYLENE EXTRACT																					
9. HYDROGEN CYANIDE (HCN)	50% ACRYLONITRILE COPRODUCT			DC			A						A								A	
9. HYDROGEN CYANIDE (HCN)	50% ANDRUSSOW PROCESS	A					A						A								A	
10. STYRENE	100% ETHYL BENZENE																					
11. 1,1,1, TRICHLOROETHANE	10% ETHANE CHLORINATION		D											A				A				
11. 1,1,1, TRICHLOROETHANE	74% VINYL CHLORIDE													A				A				
11. 1,1,1, TRICHLOROETHANE	16% VINYLIDENE CHLORIDE																	A				
12. CARBON TETRACHLORIDE	38% CARBON DISULFIDE													A								
12. CARBON TETRACHLORIDE	42% CHLOROPARAFFIN CHLORINOLYSIS			DC										A								
12. CARBON TETRACHLORIDE	20% METHANE	A												A								
13. FORMALDEHYDE	23% METAL OXIDE/METHANOL						A						A									
13. FORMALDEHYDE	77% SILVER CATALYST/METHANOL						A						A									

Table III-3. (continued)

		Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
Product	Process	1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
4. METHYL METHACRYLATE (MMA)	100% ACETONE CYANOHYDRIN																					
5. PROPYLENE OXIDE	60% CHLOROHYDRIN			BC										A								
5. PROPYLENE OXIDE	40% PEROXIDATION			BC	B		S						A									
6. PROPYLENE	54% NAPTHA/GAS OIL PYROLYSIS	A	BC	BC	BC	C																
6. PROPYLENE	16% NATURAL GAS LIQUIDS PYROLYSIS	A	BC	BC	BC	C																
6. PROPYLENE	30% REFINERY BY-PRODUCT	A	BC	BC	BC	C																
7. NITROBENZENE	100% BENZENE NITRATION																					1
18. ETHYLENE GLYCOL	100% ETHYLENE OXIDE		G																			
19. CYCLOHEXANOL/CYCLOHEXANONE	75% CYCLOHEXANE						A						A									
19. CYCLOHEXANOL/CYCLOHEXANONE	25% PHENOL								A													
20. CUMENE	100% BENZENE		BC																			
21. METHANOL (METHYL ALCOHOL)	100% METHANE	A							A	A						A						
22. PHENOL	3% CHLOROBENZENE																	A				
22. PHENOL	2% BENZENE SULFONATION																A					
22. PHENOL	93% CUMENE						A						A									
22. PHENOL	2% TOLUENE OXIDATION						A						A									
23. ANILINE	100% NITROBENZENE HYDROGENATION								A													
24. FLUOROCARBONS	100% CCL4/C2CL6 FLUORINATION																			A		
25. PERCHLOROETHYLENE	66% ETHYLENE DICHLORIDE													A								
25. PERCHLOROETHYLENE	34% ETHANE CHLORINOLYSIS													A								
26. TEREPHTHALIC ACID (TPA)	39% AMOCO						A						A									
26. TEREPHTHALIC ACID (TPA)	47% EASTMAN						A						A									
26. TEREPHTHALIC ACID (TPA)	14% MOBIL						A						A									
27. CHLOROBENZENE	100% BENZENE CHLORINATION													A								
28. ACRYLIC ACID	24% MODIFIED REPPE		CD							A						A						
28. ACRYLIC ACID	77% PROPYLENE OXIDATION			BC			A						A									
29. ACETIC ACID	33% ACETALDEHYDE		I				S						A									
29. ACETIC ACID	44% BUTANE OXIDATION				BC		S						A									
29. ACETIC ACID	19% METHANOL									A						A						
29. ACETIC ACID	4% OTHERS																					

Table III-3. (continued)

Product	Process	Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
30. CHLOROPRENE	100% VIA BUTADIENE				C									A								
31. ALKYL LEADS	5% ELECTROLYSIS	F																				
31. ALKYL LEADS	95% ETHYL CHLORIDE		F																			
32. ACETONE	69% CUMENE						A						A									
32. ACETONE	31% ISOPROPANOL						S						S									
33. ETHYL CHLORIDE	4% ETHANOL/ETHANE		BC											A								
33. ETHYL CHLORIDE	96% ETHYLENE CHLORINATION		BC											A								
34. ETHANOLAMINES	100% ETHYLENE OXIDE		G				A														S	
35. VINYL ACETATE (VA)	13% ACETYLENE VAPOR PHASE		CD																			
35. VINYL ACETATE (VA)	72% ETHYLENE VAPOR PHASE		BC					A					A									
35. VINYL ACETATE (VA)	15% ETHYLENE LIQUID PHASE		BC					A						A								
36. METHYLENE CHLORIDE	35% METHANE CHLORINATION	A												A								
36. METHYLENE CHLORIDE	45% METHANOL/METHYL CHLORIDE	F												A								
37. 1.3 BUTADIENE	80% ETHYLENE COPRODUCT	A	BC	BC	BC	C																
37. 1.3 BUTADIENE	13% N-BUTANE				B	C			S													
37. 1.3 BUTADIENE	7% N-BUTENE				C		S						S									
38. VINYLIDENE CHLORIDE	50% 1,1,1 TRICHLOROETHYLENE																					
38. VINYLIDENE CHLORIDE	50% 1,1,2 TRICHLOROETHYLENE																					
39. TOLUENE DIISOCYANATE (TDI)	100% DIAMINOTOLUENE									A												1,2
40. CHLOROFORM	61% METHANE CHLORINATION	A												A								
40. CHLOROFORM	39% METHANOL CHLORINATION													A								
41. PHTHALIC ANHYDRIDE	30% NAPTHALENE						A						A									
41. PHTHALIC ANHYDRIDE	70% O-XYLENE						A						A									
42. ISOPROPANOL (ISOPROPYL ALCOHOL)	100% PROPYLENE/SULFURIC ACID			BC																		
43. ACETIC ANHYDRIDE	100% ACETIC ACID																					3
44. GLYCEROL (SYNTHETIC ONLY)	14% ACROLEIN								A													
44. GLYCEROL (SYNTHETIC ONLY)	15% ALLYL ALCOHOL													A								
44. GLYCEROL (SYNTHETIC ONLY)	71% EPICHLOROHYDRIN			BC										A								
45. NITROPHENOL	100% PHENOL NITRATION																					

Table III-3. (continued)

Product	Process	Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Misculianeous
46. CYCLOHEXANE	84% BENZENE HYDROGENATION								A													
46. CYCLOHEXANE	16% PETROLEUM DISTILLATION																					
47. BISPHENOL A	100% PHENOL/ACETONE																					
48. CELLULOSE ACETATE	100% CELLULOSE ESTERIFICATION																					
49. CAPROLACTAM	100% CYCLOHEXANONE																				A	4
50. PENTAERYTHRITOL	100% FORMALDEHYDE/ACETALDEHYDE	T	T																			
51. NONYL PHENOL	100% PHENOL ALKYLATION																					
52. ACRYLAMIDE	100% ACRYLONITRILE																				S	
53. DIETHYLENE, TRIETHYLENE GLYCOLS	100% COPRODUCTS W/ETHYLENE GLYCOL		G																			
54. FUMARIC ACID	100% MALEIC ACID/ISOMERIZATION																					
55. PROPYLENE GLYCOLS (MONO,DI,TRI)	100% PROPYLENE OXIDE HYDRATION			G																		
56. EPICHLOROHYDRIN	100% ALLYL CHLORIDE/HCL													A								
57. ALLYL CHLORIDE	100% PROPYLENE CHLORINATION			BC										A								
58. ADIPONITRILE/HMDA	11% ACRYLONITRILE								A													
58. ADIPONITRILE/HMDA	24% ADIPIC ACID								A												A	
58. ADIPONITRILE/HMDA	65% BUTADIENE	L			C		S		A				S									
59. TRICHLOROETHYLENE	9% ACETYLENE													A								
59. TRICHLOROETHYLENE	91% ETHYLENE DICHLORIDE																	A				
60. METHYL ISOBUTYL KETONE (MIBK)	100% ACETONE								A													
61. PYRIDINE	100% FORMALDEHYDE/ACETALDEHYDE	T	I																		A	
62. BENZENE	80% NOT IN PROJECT SCOPE																					
62. BENZENE	20% TOLUENE HYDRODEALKYLATION								A													
63. ETHANOL (ETHYL ALCOHOL)	100% ETHYLENE		BC																			
64. UREA	100% AMMONIA/CARBON DIOXIDE															A					A	
65. ACETALDEHYDE	100% ETHYLENE		BC				S						A									
66. ISOPRENE	67% C4 HYDROCARBONS																					
66. ISOPRENE	33% ISOAMYLENE EXTRACTION																					
67. FURFURAL	100% POLYSACCHARIDES HYDROLYSIS																					
68. GLYCOL ETHERS	97% ETHYLENE OXIDE		G																			
68. GLYCOL ETHERS	3% PROPYLENE OXIDE																					

Table III-3. (continued)

		Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
Product	Process	1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
69. DINITROTOLUENE	100% TOLUENE DINITRATION																					
70. SEC-BUTANOL	100% BUTYLENES																					
71. LINEAR ALKYL BENZENE	100% BENZENE ALKYLATION																			A		
72. ACROLEIN	100% PROPYLENE OXIDATION			BC			A						A									
73. DIPHENYLAMINE	100% ANILINE AMINATION																	A				
74. METHYL STYRENE	15% CUMENE DEHYDROGENATION																					
74. METHYL STYRENE	85% CUMENE PROCESS BY-PRODUCT		BC																			
75. ETHYLENE DIAMINE/TRIETHYLENE TETRAMINE	100% EDC AMMONOLYSIS																	A			A	
76. ETHYL ACRYLATE	61% ACETYLENE (REPPE)		CD							A						A						
76. ETHYL ACRYLATE	39% DIRECT ESTERFICATION																					
77. METHYL CHLORIDE	2% METHANE CHLORINATION	A												A								
77. METHYL CHLORIDE	98% METHANOL HYDROCHLORINATION																	A				
78. METHYLENE DIPHENYLENE DIISOCYANATE	100% DPMDA/PHOSGENE																					2
79. N-BUTYRALDEHYDE	100% OXO PROCESS			BC					A	A												
80. NITROANILINE	100% NITRO CHLORBENZENE																				A	
81. ACETOPHENONE	60% CUMENE PEROXIDATION						A						A									
81. ACETOPHENONE	40% ETHYL BENZENE OXIDATION						A		S				A									
82. ISOPHTHALIC ACID	100% M-XYLENE OXIDATION						A						A		S							
83. BENZOIC ACID	100% TOLUENE AIR OXIDATION						A						A									
84. DIISOOCTYL PHTHALATE (DI2-ETHYLHEXYL)	100% PHTHALIC ANHYDRIDE/ALCOHOL																					
85. 2-ETHYL 1-HEXANOL	100% CONDENSATION								A	A												
86. N-BUTANOL (BUTYL ALCOHOL)	20% ACETALDEHYDE		I						A	A												
86. N-BUTANOL (BUTYL ALCOHOL)	80% OXO PROCESS			BC					A	A												
87. PROPIONIC ACID	7% OTHERS																					
87. PROPIONIC ACID	93% OXO PROCESS		BC						A	A												
88. ETHYL ACETATE	100% ACETIC ACID																					
89. ETHYLENE DIBROMIDE	100% ETHYLENE BROMINATION		BC												A							
90. ACETONE CYANOHYDRIN	100% ACETONE CYANATION																					
91. BENZYL CHLORIDE	100% TOLUENE CHLORINATION													A								

Table III-3. (continued)

Product	Process	Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
92. DICHLOROPHENOL	45% PHENOL CHLORINATION													A								
92. DICHLOROPHENOL	55% TRICHLOROBENZENE																					
93. ISOBUTYRALDEHYDE	100% OXO PROCESS			BC					A	A												
94. CRESYLIC ACIDS (SYN)	4% CYMENE OXIDATION						S						A									
94. CRESYLIC ACIDS (SYN)	80% NATURAL COAL TAR						S						S			A						
94. CRESYLIC ACIDS (SYN)	8% PHENOL/METHANOL																					
94. CRESYLIC ACIDS (SYN)	8% TOLUENE SULFONATION																					
95. N-N DIMETHYL ANILINE	100% ANILINE ALCOHOLYSIS																					
96. ACETYLENE	30% CALCIUM CARBIDE																					
96. ACETYLENE	8% ETHYLENE BY-PRODUCT	A	BC	BC	BC	C																
96. ACETYLENE	62% HYDROCARBON OXIDATION	A					A						A									
97. PHOSGENE	100% CARBON MONOXIDE/CHLORINE									A				A								
98. T-BUTANOL	21% ISOBUTYLENE				C																	
98. T-BUTANOL	79% PROPYLENE OXIDE CO-PRODUCT			BC										A								
99. SALICYLIC ACID	100% SODIUM PHENATE															A		A				
100. DIMETHYL HYDRAZINE	100% NITROSODIMETHYL AMINE						A						A								A	
101. DODECENE	100% NONENE CO-PRODUCT			BC																		
102. DIISOLDCYL PHTHALATE	100% PHTHALIC ANHYDRIDE/ISODECANOL																					
103. BUTYL ACRYLATE	100% ACRYLIC ACID ESTERIFICATION																					
104. CHLOROSULFONIC ACID	100% SO3 HYDROCHLORINATION																					
105. METHYL ETHYL KETONE (MEK)	25% BUTANE OXIDATION				BC		A						A									
105. METHYL ETHYL KETONE (MEK)	75% SEC-BUTANOL																					
106. ISOBUTANOL (ISOBUTYL ALCOHOL)	100% OXO PROCESS			BC					A	A												
107. HYDROQUINONE	100% ACETONE CO-PRODUCT						S						S									
108. MONO,DI,TRI-METHYL AMINES	100% METHANOL AMMONOLYSIS																				A	
109. ADIPIC ACID	100% CYCLOHEXANE																					1
110. CHLORONITROBENZENE	100% CHLOROBENZENE NITRATION																					1
111. CARBON DISULFIDE	100% METHANE/SULFUR VAPOR	A																				
112. BIPHENYL	100% TOLUENE HYDRODEALKYLATION								A													
113. ACET[illegible]	100% SODIUM ACETATE													A								

Table III-3. (continued)

		Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
Product	Process	1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
114. MONO,DI,TRI,ETHYL AMINE	100% ETHANOL AMMONOLYSIS																				A	
115. CHLOROACETIC ACID	100% ACETIC ACID CHLORINATION													A								
116. BENZOPHENONE	100% BENZENE/CARBON TETRACHLORIDE																	A				
117. METHYL BROMIDE	100% METHANOL/HBR AND BROMINE														S				S			
118. PROPYL ALCOHOL	87% OXO PROCESS		BC						A	A												
118. PROPYL ALCOHOL	13% PROPANE OXIDATION		BC	BC	BC		A						A									
119. BUTYL AMINES	100% BUTYRALDEHYDE HYDROGENATION	L			C				S												S	
120. ETHYL (DIETHYL) ETHER	100% ETHANOL		BC																			
121. PROPYL AMINES (M-D-T)	50% N-PROPYL ALCOHOL																				A	
121. PROPYL AMINES (M-D-T)	50% N-PROPYL CHLORIDE																				A	
122. CROTONALDEHYDE	100% ALDO PROCESS		T																			
123. ISOOCTYL ALCOHOL	100% OXO PROCESS/HYDROGENATION								A	A												
124. FORMIC ACID	98% N-BUTANE OXIDATION		BC	BC	BC		A						A									
125. ETHYLENE GLYCOL METHYL ETHYL ETHER ACETATE	100% ETHOXY ETHANOL ESTER																					
126. LINEAR ALKYL BENZENE SULFONATE	100% LAB SULFONATION																A					
127. ISODECANOL	25% N-PARAFFIN OXIDATION						A						A									
127. ISODECANOL	75% OXO PROCESS								A	A												
128. ALLYL ALCOHOL	47% ALLYL CHLORIDE HYDROLYSIS																					
128. ALLYL ALCOHOL	6% PROP GLYCOL DEHYDRATION																					
128. ALLYL ALCOHOL	47% PROP OXIDE ISOMERIZATION																					
129. ISOPROPYL ACETATE	100% ISOPROPANOL ESTERIFICATION																					
130. METHYL ACETATE	100% ACETIC ACID/METHANOL																					
131. CYCLOOCTADIENE	100% BUTADIENE DIMERIZATION																					
132. HEXACHLOROBENZENE	100% HEXACHLOROCYCLOHEXANE													A								
133. N-BUTYL ACETATE	100% ESTERIFICATION																					
134. BUTYRIC ACID	33% BUTYRALDEHYDE OXIDATION						S						A									
134. BUTYRIC ACID	67% N-BUTANE OXIDATION				BC		S						A									
135. DINITROPHENOL	100% DINITRATION OF PHENOL																					
136. AMINO ETHYLETHANOLAMINE	100% ETHYLENE OXIDE		G																			

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Table III-3. (continued)

Product	Process	Reaction-Reactant-Related Carrier Gases																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
137. CYCLOHEXYLAMINE	50% ANILINE								A													
137. CYCLOHEXYLAMINE	50% CYCLOHEXANONE								A												A	
138. TOLUENE SULFONIC ACIDS	100% TOLUENE SULFONATION																A					
139. BENZYL BENZOATE	50% BENZALDEHYDE																					
139. BENZYL BENZOATE	50% BENZYL ALCOHOL/ACID																					
140. BENZOYL CHLORIDE	100% BENZOIC ACID													A								

Legend

[a] Organic Carrier Gases

A - Methane
B - Alkanes
C - Alkenes, dienes
D - Alkynes
E - Ethers
F - Chlorinated hydrocarbons
G - Epoxides
H - Amines
I - Aldehydes
J - Esters
K - Mercaptans
L - Nitriles
M - Brominated hydrocarbons
N - Fluorinated hydrocarbons

1. Nitrogen oxides
2. Phosgene
3. Ketene
4. Hydroxylamine
5. Baron trifuluoride

[b] Inorganic Carrier Gases

A - Always found
S - Sometimes found

Table III-4. Reaction-Product-Related Gases for 140 Synthetic Organic Chemicals

Product	Process	Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
1. VINYL CHLORIDE	1% ACETYLENE		F																			
1. VINYL CHLORIDE	99% ETHYLENE DICHLORIDE		F															A				
2. ACRYLONITRILE	100% PROPYLENE OXIDATION	L								A						A						
3. ETHYLENE DICHLORIDE	50% DIRECT CHLORINATION		F																			
3. ETHYLENE DICHLORIDE	50% OXYCHLORINATION		F																			
4. MALEIC ANHYDRIDE	85% BENZENE OXIDATION									S						A						
4. MALEIC ANHYDRIDE	15% BUTANE OXIDATION									S						A						
5. ETHYLENE OXIDE	66% AIR OXIDATION/ETHYLENE		B							S						A						
5. ETHYLENE OXIDE	34% O2 OXIDATION/ETHYLENE		B													A						
6. DIMETHYL TEREPHTHALATE (DMT)	23% AMOCO VIA TEREPHTHALIC ACID									A						A						
6. DIMETHYL TEREPHTHALATE (DMT)	35% DUPONT									A						A						
6. DIMETHYL TEREPHTHALATE (DMT)	17% EASTMAN VIA TEREPHTHALIC ACID									A						A						
6. DIMETHYL TEREPHTHALATE (DMT)	25% HERCULES									A						A						
7. ETHYLENE	46% NAPTHA GAS OIL PYROLYSIS	A	BC						A													
7. ETHYLENE	52% NATURAL GAS LIQUIDS PYROLYSIS	A	BC						A													
7. ETHYLENE	2% REFINERY BY-PRODUCT	A	BC						A													
8. ETHYLBENZENE	98% BENZENE ALKYLATION																	A				
8. ETHYLBENZENE	2% MIXED XYLENE EXTRACT																					
9. HYDROGEN CYANIDE (HCN)	50% ACRYLONITRILE COPRODUCT	L								A						A						
9. HYDROGEN CYANIDE (HCN)	50% ANDRUSSOW PROCESS	L																				
10. STYRENE	100% ETHYL BENZENE													A								
11. 1,1,1, TRICHLOROETHANE	10% ETHANE CHLORINATION																	A				
11. 1,1,1, TRICHLOROETHANE	74% VINYL CHLORIDE																	A				
11. 1,1,1, TRICHLOROETHANE	16% VINYLIDENE CHLORIDE																					
12. CARBON TETRACHLORIDE	38% CARBON DISULFIDE																					
12. CARBON TETRACHLORIDE	42% CHLOROPARAFFIN CHLORINOLYSIS													A				A				
12. CARBON TETRACHLORIDE	20% METHANE	F																A				
13. FORMALDEHYDE	23% METAL OXIDE/METHANOL	I																				
13. FORMALDEHYDE	77% SILVER CATALYST/METHANOL	I																				

Table III-4. (continued)

		Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
Product	Process	1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
14. METHYL METHACRYLATE (MMA)	100% ACETONE CYANOHYDRIN	1																				
15. PROPYLENE OXIDE	60% CHLOROHYDRIN																	A				
15. PROPYLENE OXIDE	40% PEROXIDATION																					
16. PROPYLENE	54% NAPTHA/GAS OIL PYROLYSIS	A	BC	BC					A													
16. PROPYLENE	16% NATURAL GAS LIQUIDS PYROLYSIS	A	BC	BC					A													
16. PROPYLENE	30% REFINERY BY-PRODUCT	A	BC	BC					A													
17. NITROBENZENE	100% BENZENE NITRATION																					
18. ETHYLENE GLYCOL	100% ETHYLENE OXIDE																					
19. CYCLOHEXANOL/CYCLOHEXANONE	75% CYCLOHEXANE																					1
19. CYCLOHEXANOL/CYCLOHEXANONE	25% PHENOL																					
20. CUMENE	100% BENZENE																					
21. METHANOL (METHYL ALCOHOL)	100% METHANE								A	A						A						
22. PHENOL	3% CHLOROBENZENE																					
22. PHENOL	2% BENZENE SULFONATION																A					
22. PHENOL	93% CUMENE																					
22. PHENOL	2% TOLUENE OXIDATION															A						
23. ANILINE	100% NITROBENZENE HYDROGENATION																					
24. FLUOROCARBONS	100% CCL4/C2CL6 FLUORINATION	N	N															A				
25. PERCHLOROETHYLENE	66% ETHYLENE DICHLORIDE																	A				
25. PERCHLOROETHYLENE	34% ETHANE CHLORINOLYSIS																	A				
26. TEREPHTHALIC ACID (TPA)	39% AMOCO									A						A						
26. TEREPHTHALIC ACID (TPA)	47% EASTMAN									A						A						
26. TEREPHTHALIC ACID (TPA)	13% MOBIL									A						A						
27. CHLOROBENZENE	100% BENZENE CHLORINATION																	A				
28. ACRYLIC ACID	23% MODIFIED REPPE																					
28. ACRYLIC ACID	77% PROPYLENE OXIDATION															S						
29. ACETIC ACID	36% ACETALDEHYDE																					
29. ACETIC ACID	44% BUTANE OXIDATION																					
29. ACETIC ACID	19% METHANOL																					
29. ACETIC ACID	4% OTHERS								S													

Table III-4. (continued)

Product	Process	Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
30. CHLOROPRENE	100% VIA BUTADIENE															A		A				
31. ALKYL LEADS	5% ELECTROLYSIS																					
31. ALKYL LEADS	95% ETHYL CHLORIDE																	A				
32. ACETONE	69% CUMENE																					
32. ACETONE	31% ISOPROPANOL								S													
33. ETHYL CHLORIDE	4% ETHANOL/ETHANE		F															A				
33. ETHYL CHLORIDE	96% ETHYLENE CHLORINATION		F															A				
34. ETHANOLAMINES	100% ETHYLENE OXIDE																					
35. VINYL ACETATE (VA)	13% ACETYLENE VAPOR PHASE																					
35. VINYL ACETATE (VA)	72% ETHYLENE VAPOR PHASE		I													A						
35. VINYL ACETATE (VA)	15% ETHYLENE LIQUID PHASE		I													A						
36. METHYLENE CHLORIDE	35% METHANE CHLORINATION																	A				
36. METHYLENE CHLORIDE	65% METHANOL/METHYL CHLORIDE																	A				
37. 1.3 BUTADIENE	80% ETHYLENE COPRODUCT				C				A													
37. 1.3 BUTADIENE	13% N-BUTANE				C																	
37. 1.3 BUTADIENE	7% N-BUTENE				C				A													
38. VINYLIDENE CHLORIDE	50% 1,1,1 TRICHLOROETHYLENE																	A				
38. VINYLIDENE CHLORIDE	50% 1,1,2 TRICHLOROETHYLENE																	A				
39. TOLUENE DIISOCYANATE (TDI)	100% DIAMINOTOLUENE																	A				
40. CHLOROFORM	61% METHANE CHLORINATION																	A				
40. CHLOROFORM	39% METHANOL CHLORINATION															A						
41. PHTHALIC ANHYDRIDE	30% NAPTHALENE									S						A						
41. PHTHALIC ANHYDRIDE	70% O-XYLENE									S						A						
42. ISOPROPANOL (ISOPROPYL ALCOHOL)	100% PROPYLENE/SULFURIC ACID																					
43. ACETIC ANHYDRIDE	100% ACETIC ACID																					3
44. GLYCEROL (SYNTHETIC ONLY)	14% ACROLEIN																					
44. GLYCEROL (SYNTHETIC ONLY)	15% ALLYL ALCOHOL																					
44. GLYCEROL (SYNTHETIC ONLY)	71% EPICHLOROHYDRIN															A		A				
45. NITROPHENOL	100% PHENOL NITRATION																					1

Table III-4. (continued)

Product	Process	Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
46. CYCLOHEXANE	84% BENZENE HYDROGENATION																					
46. CYCLOHEXANE	16% PETROLEUM DISTILLATION																					
47. BISPHENOL A	100% PHENOL/ACETONE																					
48. CELLULOSE ACETATE	100% CELLULOSE ESTERIFICATION																					
49. CAPROLACTAM	100% CYCLOHEXANONE																					4
50. PENTAERYTHRITOL	100% FORMALDEHYDE/ACETALDEHYDE																					
51. NONYL PHENOL	100% PHENOL ALKYLATION																					5
52. ACRYLAMIDE	100% ACRYLONITRILE																					
53. DIETHYLENE, TRIETHYLENE GLYCOLS	100% COPRODUCTS W/ETHYLENE GLYCOL																					
54. FUMARIC ACID	100% MALEIC ACID/ISOMERIZATION																					
55. PROPYLENE GLYCOLS (MONO,DI,TRI)	100% PROPYLENE OXIDE HYDRATION																					
56. EPICHLOROHYDRIN	100% ALLYL CHLORIDE/HCL																					
57. ALLYL CHLORIDE	100% PROPYLENE CHLORINATION																	A				
58. ADIPONITRILE/HMDA	11% ACRYLONITRILE																					
58. ADIPONITRILE/HMDA	24% ADIPIC ACID																					
58. ADIPONITRILE/HMDA	65% BUTADIENE																					
59. TRICHLOROETHYLENE	9% ACETYLENE																	A				
59. TRICHLOROETHYLENE	91% ETHYLENE DICHLORIDE																					
60. METHYL ISOBUTYL KETONE (MIBK)	100% ACETONE																					
61. PYRIDINE	100% FORMALDEHYDE/ACETALDEHYDE								A													
62. BENZENE	80% NOT IN PROJECT SCOPE																					
62. BENZENE	20% TOLUENE HYDRODEALKYLATION	A																				
63. ETHANOL (ETHYL ALCOHOL)	100% ETHYLENE																					
64. UREA	100% AMMONIA/CARBON DIOXIDE																					
65. ACETALDEHYDE	100% ETHYLENE		I															A				
66. ISOPRENE	67% C4 HYDROCARBONS								A													
66. ISOPRENE	33% ISOAMYLENE EXTRACTION								A													
67. FURFURAL	100% POLYSACCHARIDES HYDROLYSIS																					
68. GLYCOL ETHERS	97% ETHYLENE OXIDE																					
68. GLYCOL ETHERS	3% PROPYLENE OXIDE																					

Table III-4. (continued)

Product	Process	Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
69. DINITROTOLUENE	100% TOLUENE DINITRATION																					1
70. SEC-BUTANOL	100% BUTYLENES																					
71. LINEAR ALKYL BENZENE	100% BENZENE ALKYLATION								A													
72. ACROLEIN	100% PROPYLENE OXIDATION									S						S						
73. DIPHENYLAMINE	100% ANILINE AMINATION																					
74. METHYL STYRENE	15% CUMENE DEHYDROGENATION								A													
74. METHYL STYRENE	85% CUMENE PROCESS BY-PRODUCT																					
75. ETHYLENE DIAMINE/TRIETHYLENE TETRAMINE	100% EDC AMMONOLYSIS																					
76. ETHYL ACRYLATE	61% ACETYLENE (REPPE)																					
76. ETHYL ACRYLATE	39% DIRECT ESTERFICATION																					
77. METHYL CHLORIDE	2% METHANE CHLORINATION	F																				
77. METHYL CHLORIDE	98% METHANOL HYDROCHLORINATION	F																				
78. METHYLENE DIPHENYLENE DIISOCYANATE	100% DPMDA/PHOSGENE																					
79. N-BUTYRALDEHYDE	100% OXO PROCESS																					
80. NITROANILINE	100% NITRO CHLORBENZENE																					
81. ACETOPHENONE	60% CUMENE PEROXIDATION																					
81. ACETOPHENONE	40% ETHYL BENZENE OXIDATION																					
82. ISOPHTHALIC ACID	100% M-XYLENE OXIDATION																					
83. BENZOIC ACID	100% TOLUENE AIR OXIDATION																					
84. DIISOOCTYL PHTHALATE (DI2-ETHYLHEXYL)	100% PHTHALIC ANHYDRIDE/ALCOHOL																					
85. 2-ETHYL 1-HEXANOL	100% CONDENSATION																					
86. N-BUTANOL (BUTYL ALCOHOL)	20% ACETALDEHYDE																					
86. N-BUTANOL (BUTYL ALCOHOL)	80% OXO PROCESS																					
87. PROPIONIC ACID	7% OTHERS																					
87. PROPIONIC ACID	93% OXO PROCESS																					
88. ETHYL ACETATE	100% ACETIC ACID																					
89. ETHYLENE DIBROMIDE	100% ETHYLENE BROMINATION																					
90. ACETONE CYANOHYDRIN	100% ACETONE CYANATION																					
91. BENZYL CHLORIDE	100% TOLUENE CHLORINATION																A					

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Table III-4. (continued)

Product	Process	Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
92. DICHLOROPHENOL	45% PHENOL CHLORINATION																	A				
92. DICHLOROPHENOL	55% TRICHLOROBENZENE																	A				
93. ISOBUTYRALDEHYDE	100% OXO PROCESS																					
94. CRESYLIC ACIDS (SYN)	4% CYMENE OXIDATION																					
94. CRESYLIC ACIDS (SYN)	80% NATURAL COAL TAR																					
94. CRESYLIC ACIDS (SYN)	8% PHENOL/METHANOL																					
94. CRESYLIC ACIDS (SYN)	8% TOLUENE SULFONATION																					
95. N-N DIMETHYL ANILINE	100% ANILINE ALCOHOLYSIS																					
96. ACETYLENE	30% CALCIUM CARBIDE		D																			
96. ACETYLENE	8% ETHYLENE BY-PRODUCT	A	DD						A													
96. ACETYLENE	62% HYDROCARBON OXIDATION		D						A	A												
97. PHOSGENE	100% CARBON MONOXIDE/CHLORINE	F																				2
98. T-BUTANOL	21% ISOBUTYLENE																					
98. T-BUTANOL	79% PROPYLENE OXIDE CO-PRODUCT												A									
99. SALICYLIC ACID	100% SODIUM PHENATE																					
100. DIMETHYL HYDRAZINE	100% NITROSODIMETHYL AMINE																					
101. DODECENE	100% NONENE CO-PRODUCT																					
102. DIISODECYL PHTHALATE	100% PHTHALIC ANHYDRIDE/ISODECANOL																					
103. BUTYL ACRYLATE	100% ACRYLIC ACID ESTERIFICATION																					
104. CHLOROSULFONIC ACID	100% SO3 HYDROCHLORINATION																					
105. METHYL ETHYL KETONE (MEK)	25% BUTANE OXIDATION																					
105. METHYL ETHYL KETONE (MEK)	75% SEC-BUTANOL								A													
106. ISOBUTANOL (ISOBUTYL ALCOHOL)	100% OXO PROCESS																					
107. HYDROQUINONE	100% ACETONE CO-PRODUCT								S													
108. MONO,DI,TRI,METHYL AMINES	100% METHANOL AMMONOLYSIS	M																				
109. ADIPIC ACID	100% CYCLOHEXANE																					
110. CHLORONITROBENZENE	100% CHLOROBENZENE NITRATION																					
111. CARBON DISULFIDE	100% METHANE/SULFUR VAPOR																					
112. DIPHENYL	100% TOLUENE HYDRODEALKYLATION	A																				
113. ACETYL CHLORIDE	100% SODIUM ACETATE																	A				

Table III-4. (continued)

		Reaction-Product-Related Carrier Gas																				
		Organic[a]					Inorganic[b]															
Product	Process	1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
114. MONO,DI,TRI,ETHYL AMINE	100% ETHANOL AMMONOLYSIS																					
115. CHLOROACETIC ACID	100% ACETIC ACID CHLORINATION																	A				
116. BENZOPHENONE	100% BENZENE/CARBON TETRACHLORIDE																	A				
117. METHYL BROMIDE	100% METHANOL/HBR AND BROMINE	M																				
118. PROPYL ALCOHOL	87% OXO PROLESS																					
118. PROPYL ALCOHOL	13% PROPANE OXIDATION																					
119. BUTYL AMINES	100% BUTYRALDEHYDE HYDROGENATION																					
120. ETHYL (DIETHYL) ETHER	100% ETHANOL																					
121. PROPYL AMINES (M-D-T)	50% N-PROPYL ALCOHOL																					
121. PROPYL AMINES (M-D-T)	50% N-PROPYL CHLORIDE																					
122. CROTONALDEHYDE	100% ALDO PROCESS																					
123. ISOOCTYL ALCOHOL	100% OXO PROCESS/HYDROGENATION																					
124. FORMIC ACID	98% N-BUTANE OXIDATION		J																			
125. ETHYLENE GLYCOL METHYL ETHYL ETHER ACETATE	100% ETHOXY ETHANOL ESTER																					
126. LINEAR ALKYL BENZENE SULFONATE	100% LAB SULFONATION																					
127. ISODECANOL	25% N-PARAFFIN OXIDATION																					
127. ISODECANOL	75% OXO PROCESS																					
128. ALLYL ALCOHOL	47% ALLYL CHLORIDE HYDROLYSIS																					
128. ALLYL ALCOHOL	6% PROP GLYCOL DEHYDRATION																					
128. ALLYL ALCOHOL	47% PROP OXIDE ISOMERIZATION																					
129. ISOPROPYL ACETATE	100% ISOPROPANOL ESTERIFICATION																					
130. METHYL ACETATE	100% ACETIC ACID/METHANOL																					
131. CYCLOOCTADIENE	100% BUTADIENE DIMERIZATION								A													
132. HEXACHLOROBENZENE	100% HEXACHLOROCYCLOHEXANE								A									A				
133. N-BUTYL ACETATE	100% ESTERIFICATION																					
134. BUTYRIC ACID	33% BUTYRALDEHYDE OXIDATION																					
134. BUTYRIC ACID	67% N-BUTANE OXIDATION																					
135. DINITROPHENOL	100% DINITRATION OF PHENOL																					1
136. AMINO ETHYLETHANOLAMINE	100% ETHYLENE OXIDE																	S				

Table III-4. (continued)

Product	Process	Reaction-Product-Related Carrier Gas																						
		Organic[a]					Inorganic[b]																	
		1 Carbon Atom	2 Carbon Atoms	3 Carbon Atoms	4 Carbon Atoms	5 Carbon Atoms	Nitrogen	Argon	Hydrogen	Carbon Monoxide	Sulfur Dioxide	Hydrogen Sulfide	Oxygen	Chlorine	Bromine	Carbon Dioxide	Sulfur Trioxide	Hydrogen Chloride	Hydrogen Bromide	Hydrogen Fluoride	Ammonia	Miscellaneous
137. CYCLOHEXYLAMINE	50% ANILINE																					
137. CYCLOHEXYLAMINE	50% CYCLOHEXANONE																					
138. TOLUENE SULFONIC ACIDS	100% TOLUENE SULFONATION																					
139. BENZYL BENZOATE	50% BENZALDEHYDE																					
139. BENZYL BENZOATE	50% BENZYL ALCOHOL/ACID																					
140. BENZOYL CHLORIDE	100% BENZOIC ACID																A				

Legend

[a] Organic Carrier Gases
- A - Methane
- B - Alkanes
- C - Alkenes, dienes
- D - Alkynes
- E - Ethers
- F - Chlorinated hydrocarbons
- G - Epoxides
- H - Amines
- I - Aldehydes
- J - Esters
- K - Mercaptans
- L - Nitriles
- M - Brominated hydrocarbons
- N - Fluorinated hydrocarbons

1. Nitrogen oxides
2. Phosgene
3. Ketene
4. Hydroxylamine
5. Boron trifluoride

[b] Inorganic Carrier Gases
- A - Always found
- S - Sometimes found

categorized. The tables in Appendix C are useful for locating reactions with common carrier gases.

Carrier gases generated by reaction reactants or products are not the sole source of reaction-related carrier gases. Another source of reaction-related carrier gases is gases introduced with liquid or solid reactants or generated through decomposition of liquid or solid products.

Carrier gases introduced with liquid or solid reactants are dissolved in, are adsorbed on, or exist in an ionized or salt form in the liquid or solid reactant. Table III-5 gives data on the gas flow resulting from 100% of the gases dissolved in several organic liquids. These flow rates are based on 100 million lb of the liquid being introduced into the reactor per year and on the liquid being saturated with gas. It is evident that carrier gases introduced in this fashion are normally not significant contributors to the total carrier-gas flow.

Water can also introduce dissolved gases into a reactor. Table III-6[2] gives the amount of carrier gas that can be expected when water is fed at various temperatures into a system. Although it is possible for reactions to use more than 1000 gpm of water, this is a fairly high flow. For these flows the absorbed gas represents a carrier-gas flow contribution of low significance.

Gases adsorbed on solids can be a significant contribution to carrier-gas flow only under certain circumstances. A solid that adsorbs a great deal of gas, such as activated carbon, can carry 0.1 to 5 scf of gas/lb of solid, and if this solid is fed to a reactor that has had the appropriate conditions to desorb the gases from the carbon (higher temperatures or lower pressures), the gas can be released as a carrier gas.[3] Normal chemical solids, however, have much less capacity to adsorb gases and are normally not significant sources of carrier gases.

Gases that can be generated by chemical conversion of an ionic or salt form can be significant sources of carrier gases. Sodium carbonate, for instance, that is acidified can generate about 3.4 scf of CO_2/lb of dry Na_2CO_3 fed. Acidification of sodium sulfide can generate about 4.6 scf of H_2S/lb of dry sodium

Table III-5. Contribution of Carrier Gases from Dissolved Gases in Organic Liquids[a]

	Gas Flow[b] [scfm/(100 $\bar{M}$ lb of liquid/yr)]			
Organic Liquid	H_2	N_2	CH_4	CO_2
n-Perfluoroheptane	0.25	0.68	1.45	3.68
n-Heptane	0.47			8.26
Carbon tetrachloride	0.14	0.28	1.26	4.75
Carbon disulfide	0.13	0.20	1.18	2.95
Acetone	0.27	0.70	2.63	

[a] Adapted from ref 1.

[b] At 25°C and atmospheric pressure.

Table III-6. Contribution of Carrier Gases from Gases Dissolved in Water Fed to a Reactor[a]

	Gas Flow for 1000-gpm Water	
Water Temperature (°F)	(lb/hr)	(scfm)
40	16.8	3.47
50	14.9	3.07
60	13.2	2.72
70	11.8	2.43
80	10.7	2.21
90	9.7	2.00
100	8.8	1.82

[a] From ref 2.

sulfide fed. Reactions operating under conditions to free acid or basic gases from solids or liquids are not that common in SOCMI but can lead to carrier-gas formation.

Reaction-related carrier gases can result from the decomposition of liquid or solid products that form gases. The estimation of flow from this source requires specific information concerning the potential of decomposition in each case. However, the following simple order-of-magnitude case can be estimated for gases generated by chemical decomposition: a chemical with a molecular weight of 100 is being processed in vacuum equipment at the rate of 1 to 1000 lb/hr; 10 mole % of this material is decomposed to a gas. The number of moles of gas produced is equal to the number of moles of chemical decomposed. The data from the calculation are presented in Table III-7.[4] Carrier-gas generation resulting from chemical decomposition becomes significant only for very large plants or when more than 10 mole % of the chemical is being decomposed.

4. Nonreaction-Related Carrier Gases

Nonreaction-related carrier gases arise from either the planned or the unavoidable introduction of carrier gases into process equipment. If these gases are not converted to nongaseous compounds or if they change state through condensation, solution, or other physical process, they are emitted as carrier gases.

Nonreaction-related carrier gases can be classified into three areas: gases introduced to control conditions, gases introduced to control the chemical atmosphere, and gases related to reduced pressure.

Some of the gases introduced to control conditions are air, nitrogen, carbon dioxide, or methane fed to process equipment to increase or control pressure or temperature. A common example of this type of carrier gas is the air or nitrogen bled into a vacuum distillation unit for the purpose of controlling the vacuum. An evaluation of the emissions from vacuum equipment is presented in the vacuum system emission projections report. A special case of this classification is the use of gases to control the process-equipment pressure, resulting in fluid transfer operations. The gases introduced or removed to form slightly elevated or reduced pressure often result in an air emission. Al-

Table III-7. Gas Flow from Chemical Decomposition
(Equimolar Gas Evolving from 10 mole % of the Feed Decomposed)

Feed Rate		Decomposition Gas Rate	
(lb-moles/hr)	(lb/hr)[a]	(lb-mole/hr)	(scfm)
0.01	1	0.001	0.006
0.1	10	0.01	0.06
1.0	100	0.1	0.6
10.0	1000	1.0	6.0

[a] Based on a molecular weight of 100.

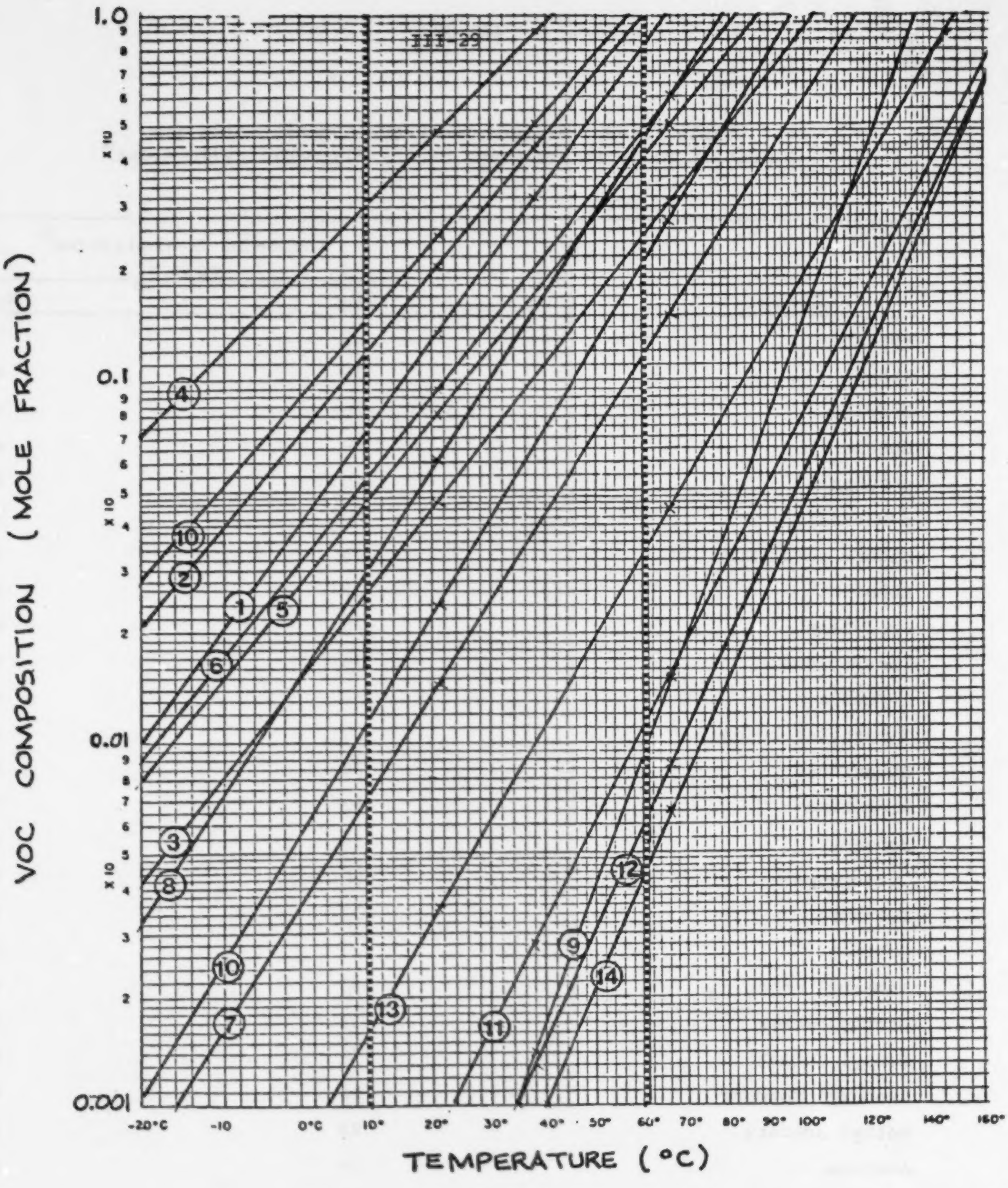
though the carrier-gas flow from the sources is small, it can be a significant fraction of the flow.

Gases introduced to control the chemical atmosphere are fed to chemical process equipment in order to modify the chemical composition of the gas or vapor phase in the equipment. This is done to promote specific reactions, to control chemical decomposition, or to prevent the hazards of operating chemical equipment in the flammable range (organic-oxygen ratio such that detonation or deflagration can occur). Inert gases such as nitrogen and carbon dioxide (CO_2 is inert to oxidation) and organic carrier gases such as methane are often used for this purpose. Table III-8 gives some data on the concentrations of inert gases required to completely prevent flammable conditions in process equipment. Since the amount of inert gas required depends on the amount of air or oxygen present, the ratic of inert gas volume to air volume can be calculated. Ranges for this ratio are listed in Table III-9. This source of carrier gases can be significant.

Gases related to reduced-pressure operation are involved in the operation of vacuum equipment. This type of carrier gas is introduced as the result of air leaking into the equipment under reduced pressure. Even though leakage can be minimized through appropriate design, it is very difficult to eliminate air leakage in vacuum equipment. Since air leakage introduces oxygen into the process vessel, sometimes inert gases must be used to prevent product decomposition or operation in the explosion range. Further information on carrier-gas flow from vacuum equipment may be found in the vacuum system emission projection report. In general carrier-gas flow from reduced pressure can be a significant fraction of the total emission.

C. VOC CONCENTRATION

Once a carrier gas is generated and reaches the emission point without being reduced through reaction or physical change, a VOC emission will occur only if the carrier gas is organic and is considered to be VOC and/or the carrier gas contacts volatile organic liquids or solids before they are emitted. In the latter case the significance of the emission depends on the mole fraction of the volatile organics in the emission, which, in turn, depends on the vapor pressure of the organics, the temperature and pressure in the process equip-



1. Methanol
2. Chloroform
3. Formic acid
4. Dichloromethane
5. Trichloroethylene
6. Acetonitrile
7. Acetic acid
8. Ethanol
9. Monoethanolamine
10. Allyl alcohol
11. Butyric acid
12. Phenol
13. Methyl phenyl ether
14. o-Cresol

Fig. III-2 . Composition of Gases Saturated with Various Compounds

Table III-8. Minimum Inert-Gas Concentration for Operation To Be Entirely Out of the Flammability Envelope[a]

Compound	Inert-Gas Concentration[b] (mole %)	
	CO_2	N_2
Methane	23	37
Ethane	31	44
Propane	28	43
Butane	28	40
n-Pentane	29	42
n-Hexane	29	42
Higher paraffins	28	42
Ethylene	39	49
Propylene	28	42
Isobutylene	26	40
1-Butene	31	44
3-Methyl-1-butene	31	44
Butadiene	35	48
Acetylene	53	65
Benzene	29	43
Cyclopropane	30	41
Methanol	32	46
Ethanol	33	45
Dimethyl ether	33	48
Diethyl ether	34	49
Methyl formate	33	45
Isobutyl formate	26	40
Methyl acetate	29	44
Acetone	28	43
Methyl ethyl ketone	34	45
Hydrogen sulfide	30	
Hydrogen	56	72
Carbon monoxide	41	58

[a] See ref 4.

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[b] Does not include the inert gas related to the air concentration. Values expressed are for mixture at 25°C and 760 mm Hg. Operation under vacuum will not require as high inert concentration as those expressed.

Table III-9. Inert-Gas-Flow Estimates to Prevent Operation in the Flammability Range[a]

	Volume of Inert Gas Required for Each Volume of Air	
	At 25°C	At 100 to 150°C
Organic gases and vapors	0.25—1	3—10
Flammable inorganic gases and acetylene	0.8—3	5—10

[a] From ref 4 for use in estimating emission rates only; not to be used for equipment design.

ment, and the degree to which the VOC achieves saturation. This is more completely descussed in the next chapter.

Estimation of the VOC concentration requires specific process details and is very difficult to generalize. In addition the vapor pressure of organic compounds varies greatly. Figure III-2 shows the saturation concentration of several organic components in a carrier gas. It is clear that VOC concentrations can vary from nearly zero to 100%.

It is not always necessary to know the exact VOC concentration. The generic approach accepts the inherent physical variability in the emission through the reality that, for a given class of reactions, the VOC concentration could be very high, moderate, or low, depending on the reaction and the specific process. Regulations covering this class of reactions would reflect this variability.

IV. CHLORINATION REACTIONS

In this chapter the development of a technique for estimation of the likely range of organic emissions from chemical reactions is concluded. This technique will be developed with chlorination reactions used as an example. The same approach should be applicable in the estimation of organic emissions from other chemical reactions.

Chlorination reactions are widely used in SOCMI. They make use of gaseous chlorine, aqueous hypochlorous acid solutions, or other chlorinating agents to substitute chlorine for other functional groups. Table IV-1 lists the products that use chlorination reactions in the group of 140 products ranked.

A. ESTIMATION OF TOTAL FLOW

The general equation for chlorination is

$$aR + bCl_2 \longrightarrow cRCl + dHCl \qquad (IV\text{-}1)$$

The minimum amount of chlorine used is dependent on the reaction stoichiometry although excess chlorine can be used. In many reactions hydrogen chloride gas is generated. In reactions that operate in the aqueous phase hydrochloric acid or a chloride salt is formed. The molar chlorine ratio (MCR) of chlorine reactant to chlorinated product can be written as the ratio of b to c or b/c. The molar ratio of HCl formed (MHCR) to product is d/c. These two ratios then give a measure of the chlorine fed and the hydrogen chloride generated in a chlorination reaction as functions of the chlorinated product produced. All these ratios are shown in Table IV-2. In addition some of the chlorination reactions use gaseous organic reactants or generate gaseous organic products; they are expressed as a/c (the molar ratio of gaseous organic reactant to product, or MGRR) for the cases of organic reactants and c/c (the molar ratio of gaseous organic product to product manufactured, or MGPR), or 1 for organic products (c/c can be a low fraction if gaseous by-products are generated), and are also shown in Table IV-2.

Once the stoichiometric relationships are known, estimation of the total carrier-gas flow from the reaction depends on knowledge of the purity of the

Table IV-1. Products That Use Chlorination Reactions

Product		Processes[a]
3.	Ethylene dichloride	50% Direct chlorination
11.	1,1,1-Trichloroethane	74% Vinyl chloride
11.	1,1,1-Trichloroethane	10% Ethane chlorination
12.	Carbon tetrachloride	42% Chloroparaffin chlorinolysis
12.	Carbon tetrachloride	20% Methane
12.	Carbon tetrachloride	38% Carbon disulfide
15.	Propylene oxide	60% Chlorohydrin
25.	Perchloroethylene	34% Ethane chlorinolysis
25.	Perchloroethylene	66% Ethylene dichloride
27.	Chlorobenzene	100% Benzene chlorination
30.	Chloroprene	100% Via butadiene
33.	Ethyl chloride	4% Ethanol/ethane
36.	Methylene chloride	65% Methanol/methyl chloride
36.	Methylene chloride	35% Methane chlorination
40.	Chloroform	39% Methanol chlorination
40.	Chloroform	61% Methane chlorination
44.	Glycerol (synthetic only)	71% Epichlorohydrin
57.	Allyl chloride	100% Propylene chlorination
59.	Trichloroethylene	9% Acetylene
77.	Methyl chloride	2% Methane chlorination
91.	Benzyl chloride	100% Toluene chlorination
92.	Dichlorophenol	45% Phenol chlorination
97.	Phosgene	100% Carbon monoxide/chlorine
113.	Acetyl chloride	100% Sodium acetate
115.	Chloroacetic acid	100% Acetic acid chlorination
132.	Hexachlorobenzene	100% Hexachlorocyclohexane from benzene

[a] Percentages listed indicate the estimated portion of the domestic production manufactured by that process.

Table IV-2. Stoichiometric Ratios of Potential Carrier Gases to the Chlorination Product

Product	Major Organic Reactant	Molar Chlorine Ratio (MCR)	Molar Hydrogen Chloride Ratio (MHCR)	Molar Gaseous Reactant Ratio (MGRR)	Molar Gaseous Product Ratio (MGPR)
Ethylene dichloride	Ethylene	1	0	1	0 (0.1)[a]
1,1,1-Trichloroethane	Vinyl chloride	1	0	0	0
	Ethane	3	1—3[b]	1	1/3
Carbon tetrachloride	Propane-propylene	7—8[c]	6—8[c]	1	0 (0.1)[a]
	Methane	4	4	1	0[d]
	Carbon disulfide	2	0	0	0
Propylene oxide	Propylene (chlorohydrin)	1	1	1	0
Perchloroethylene	Propane-propylene	7/2—8	4—8	1	0
Chlorobenzene	Benzene	1	1	0	0
Chloroprene	Butadiene	1	0	1	0
Ethyl chloride	Ethanol-ethane	1/2—1	0—1	1/2—1[e]	1
Methylene chloride	Methanol—methyl chloride	1/2—1	0—1	1/2—1[f]	0
	Methane	2	2	1	0[d]
Chloroform	Methane	3	3	1	0[d]
	Acetone	3[g]	0	0	0
Glycerin (epichlorohydrin)	Allyl chloride	1[g]	0	0	0
Allyl chloride	Propylene	1	1	1	0 (0.1)[a]
Trichloroethylene	Acetylene	2	0—1[h]	1	0
Methyl chloride	Methane	1	1	1	1
Benzyl chloride(s)	Toluene	1—3	1—3	0	0
Dichlorophenol	Phenol	2	2	0	0
Phosgene	Carbon monoxide	1	0	1	1
Acetyl chloride	Sodium acetate—acetic acid	0[i]	0	0	0
Chloroacetic acid	Acetic acid	1	1	0	0
Hexachlorobenzene	Hexachlorocyclohexane from benzene	3	0	0	0

[a] Potential for formation of ethyl chloride by-product.

[b] Depending on ethylene hydrochlorination side reaction.

[c] Depending on propane-propylene ratio.

[d] Potential for formation of methyl chloride by-product.

[e] Depending on ethane-ethanol feed ratio.

[f] Depending on methyl chloride—methanol feed ratio.

[g] Used as an aqueous bleach solution.

[h] HCl formed through dehydrochlorination reaction has MHCR of 1.

[i] Uses phosphorus trichloride as a chlorinating agent.

reactants, the extent of separation of the product and excess reactants, and the existence of other carrier-gas mechanisms. The molar ratio of total reaction-related carrier-gas flow to production rate is given by Eq. (IV-2):

$$G = C + H + R + P \quad , \qquad \text{(IV-2)}$$

where

G = the molar ratio of total reaction-related carrier-gas flow from the reactor after any separation-recovery equipment to the production rate,

C = the molar ratio of chlorine-related carrier-gas flow to the production rate,

H = the molar ratio of hydrogen chloride—related carrier-gas flow to the production rate,

R = the molar ratio of gaseous organic reactants carrier-gas flow to the production rate,

P = the molar ratio of gaseous organic products carrier-gas flow to the production rate.

In turn the molar ratio of chlorine related carrier gases, C, is expressed as

$$C = \left[MCR \times (F_C - 1) \times (1 - S_C)\right] + \left[MCR \times (1 - P_C) \times F_C \times (1 - S_{In})\right] \qquad \text{(IV-3)}$$

$$(F_C - 1 = 0 \text{ if } F_C \leq 1),$$

where

MCR = the molar ratio of chlorine to product,

P_C = the molar purity of the chlorine,

F_C = the molar ratio of total chlorine feed to the stoichiometric requirement,

S_C = the separation efficiency of chlorine in the separation-recovery equipment following the reaction,

S_{In} = the separation efficiency of the gaseous impurities in the chlorine in the separation-recovery equipment following the reaction.

The molar ratio of hydrogen chloride—related carrier gases, H, is

$$H = MCHR \times (1 - S_H) \quad , \qquad \text{(IV-4)}$$

where MCHR = the molar ratio of hydrogen chloride to product, and S_H is the separation efficiency of hydrogen chloride in the separation-recovery equipment following the reaction.

The molar ratio of gaseous organic reactant carrier gases, R, is

$$R = MGRR \times F_{GR} \times (1 - Y_{GR}) \times (1 - S_{GR}) \quad , \qquad \text{(IV-5)}$$

where

MGRR = the molar ratio of gaseous organic reactant to product,

F_{GR} = the molar ratio of total gaseous organic reactant to the stoichiometric requirement,

Y_{GR} = the molar overall reaction yield on the gaseous organic reactants,

S_{GR} = the separation efficiency of the gaseous organic reactants in the separation-recovery equipment following the reaction.

The molar ratio of gaseous organic product carrier gases, P, is given as

$$P = MGPR \times (1 - S_{GP}) \quad , \qquad \text{(IV-6)}$$

where MGPR is the molar ratio of gaseous organic product to product manufactured, and S_{GP} is the separation efficiency of the gaseous organic products in the separation-recovery equipment following the reaction.

The estimation or development of all these specific variables is a major task, since many of them are defined only with specific knowledge of the design and operation of each production facility. However, since the requirements of the generic standard approach are to estimate the range of emissions from a type of reaction (i.e., the maximum and minimum carrier-gas flow from a chlorination reaction), generalization of the ranges of these variables is acceptable. The rationale for these generalizations follows: Chlorine purity (P_C) depends on whether the chlorine used is merchant chlorine or is produced and used captively at a plant site. Merchant chlorine is purified to large extent to remove

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gaseous impurities such as carbon dioxide, oxygen, and nitrogen. The purity of merchant chlorine varies from producer to producer but ranges from 97.5—99.4 mole % or better.[5,6] Purities for captive use are normally confidential to the companies. The purity of captive chlorine could range from 90 to 99 mole %. Chlorine used captively could also undergo significant purification.

The excess chlorine fed to a reactor, F_C, is also sensitive information. Chlorination reactors may recycle their gaseous products except for a purge to eliminate HCl, inert gases introduced with chlorine, and the products. F_C is based on all the products, co-products, and by-products produced. If the recycle ratio is very high (as in the case of chlorination of liquid reactants to make liquid products) or if the chlorine reacts with very high conversion to the main product, F_C approaches 1. If the recycle ratio is very low or zero or if the conversion of chlorine to the major product is low, with co-products or byproducts produced, the value of F_C would be greater than 1. If chlorine can be introduced from another source (say a chlorinated hydrocarbon feed), it is also possible for F_C to be less than 1. Values presented in Table IV-3 are based on these guidelines and also on other references.[7—17] [The term $F_C - 1$ in Eq. (IV-3) is restricted to zero or positive numbers since it is not reasonable for the first term in this equation to be negative, physically representing a negative carrier-gas production.]

The separation of unreacted chlorine, as represented by S_C, is usually accomplished in water or caustic absorbers. Design of these absorbers can vary greatly. However, a chlorine separation efficiency of 95 to 99.9% is assumed in this report.

Inert gases entering with the chlorine are difficult to remove by absorption in the HCl or chlorine absorbers. These gases (carbon dioxide, oxygen, and nitrogen) would have a low separation efficiency, S_{In}; 10 to 50% removal is assumed.

The removal efficiency of HCl, S_H, depends on whether HCl is recovered as a concentrated acid solution or is converted to sodium chloride in a caustic absorber; 90 to 99% removal is assumed.

Table IV-3. Important Variables for Estimating Organic Emissions from Chlorination Reactions

Product	Organic Reactant	P_C		F_C	F_{GR}	S_C	S_{In}	S_H	S_{CR}	S_{CP}	Y_{CR}
		Captive	Merchant								
Ethylene dichloride	Ethylene	0.9—0.99	0.975—0.994	1.0—1.1	1.01—1.1	0.95—0.999	0.1—0.5		0.1—0.9	0.1—0.9	0.9—0.95
1,1,1-Trichloroethane	Vinyl chloride	0.9—0.99	0.975—0.994	0.9—1.1		0.95—0.999	0.1—0.5		0.1—0.9		
	Ethane	0.9—0.99	0.975—0.994	1.0—1.3	0.9—1.0	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9	0.1—0.9	0.8—0.99
Carbon tetrachloride	Propane-propylene	0.9—0.99	0.975—0.994	0.7—1.0	0.8—1.0	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9	0.1—0.9	0.8—0.99
	Methane	0.9—0.99	0.975—0.994	1.0—1.01	1.0—1.6	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.5—0.99
	Carbon disulfide	0.9—0.99	0.975—0.994	1.0—1.3		0.95—0.999	0.1—0.5				
Propylene oxide (chlorohydrin)	Propylene	0.9—0.99	0.975—0.994	1.0—2.0	1.0—1.1	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.8—0.99
Perchloroethylene	Propane-propylene	0.9—0.99	0.975—0.994	0.7—1.0	0.8—1.1	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.8—0.99
Chlorobenzene	Benzene	0.9—0.99	0.975—0.994	1.0—1.4		0.95—0.999	0.1—0.5	0.9—0.99			
Chloroprene	Butadiene	0.9—0.99	0.975—0.994	1.0—1.4	1.0—1.1	0.95—0.999	0.1—0.5		0.1—0.9		0.9—0.99
Ethyl chloride	Ethanol-ethane	0.9—0.99	0.975—0.994	1.0—1.1	1.0—1.1	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9	0.9—0.99	0.9—0.99
Methylene chloride	Methanol—methyl chloride	0.9—0.99	0.975—0.994	1.0—1.01	1.0—1.1	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.9—0.99
	Methane	0.9—0.99	0.975—0.994	1.0—1.01	1.0—1.6	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.5—0.99
Chloroform	Methane	0.9—0.99	0.975—0.994	1.0—1.01	1.0—1.6	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.5—0.99
	Acetone	0.9—0.99	0.975—0.994	1.0		0.95—0.999	0.1—0.5				
Glycerin	Allyl chloride	0.9—0.99	0.975—0.994	1.0—1.22		0.95—0.999	0.1—0.5				
Allyl chloride	Propylene	0.9—0.99	0.975—0.994	1.0—1.5	1.0—1.4	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9	0.1—0.9	0.85—0.95
Trichloroethylene	Acetylene	0.9—0.99	0.975—0.994	1.0—1.1	1.0—1.1	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9	0.9—0.99	0.5—0.99
Methyl chloride	Methane	0.9—0.99	0.975—0.994	1.0—1.01	1.0—1.6	0.95—0.999	0.1—0.5	0.9—0.99	0.1—0.9		0.5—0.99
Benzyl chlorides	Toluene	0.9—0.99	0.975—0.994	1.0—1.1		0.95—0.999	0.1—0.5	0.9—0.99			
Dichlorophenol	Phenol	0.9—0.99	0.975—0.994	1.0—1.4		0.95—0.999	0.1—0.5	0.9—0.99			
Phosgene	Carbon monoxide	0.9—0.99	0.975—0.994	1.0—1.004	1.0	0.95—0.999	0.1—0.5		0.1—0.9	0.95—0.99	0.95—0.99
Acetyl chloride	Sodium acetate—acetic acid	0.9—0.99	0.975—0.994								
Chloroacetic acid	Acetic acid	0.9—0.99	0.975—0.994	1.0—1.08		0.95—0.999	0.1—0.5	0.9—0.99			
Hexachlorobenzene	Benzene	0.9—0.99	0.975—0.994	1.0—1.4		0.95—0.999	0.1—0.5				

The molar ratio of total gaseous organic reactant to the stoichometic requirement, F_{GR}, depends on the purity of the gaseous reactant. Most organic gases that are purchased have a purity in excess of 99 mole %, including ethylene, propylene, butadiene, and others. Acetylene has a somewhat lower purity (97 mole %) but can be purified to greater than 99 mole %. The purity of methane (natural gas) can vary widely (46 to 96.9% mole %), and purification processes can increase its purity. Ethane may have lower purity (94 mole %). Companies that manufacture organic gases can design chlorination processes to accept gases of much lower quality than those cited here. They can also choose to pretreat gases to increase their purity. Therefore a wide range was used to calculate the organic reactant carrier gases shown in Table IV-3.[18—23] The yields of the organic feed gases also depends on the reactant purity. Ethylene with high levels of ethane will have a lower yield (Y_{GR}) if the ethane does not take part in the reaction. These values are also shown in Table IV-3.

The separation efficiency of the unreacted gaseous reactants (S_{GR}) varies, depending on the type of organic recovery process equipment available. Reactants with high water solubilities may have a high value for S_{GR}, whereas organics with low water solubilities will have a low S_{GR} value unless a special hydrocarbon absorber (for example) is included. Values assumed for S_{GR} are from 10 to 90%.

The separation efficiency for the gaseous products and by-products (S_{GP}) depends on whether recovery of the product or by-product is economically feasible. Values for S_{GP} vary from 10 to 99%.

Chlorinated products normally have a low tendency to form flammable mixtures and are not expected to require inert gases to prevent explosions. (However, diluents can be added for other reasons.) They are also relatively stable to oxidation and probably do not require blanketing to prevent decomposition. No chlorinated reactions in the products studied are known to operate under reduced pressure. Transfer operations might introduce carrier gases, but the volume of gas is expected to be small. Carrier-gas contribution from all these sources is assumed to be negligible for chlorination reactions. Carrier-gas flows for chlorination reactions are presented in Table IV-4.

Table IV-4. Projected Uncontrolled VOC Emission Ranges from Chlorination Reactors

Product	Major Organic Reactant	Most Volatile Liquid Organic	Carrier-Gas Flow [scfm/($\bar{M}$ lb/yr)][a] Min Max
1. Ethylene dichloride	Ethylene	Ethylene dichloride	0.056—2.02
2. 1,1,1-Trichloroethane	Vinyl chloride	1,1,1-Trichloroethane	0.014—0.53
	Ethane	1,1,1-Trichloroethane	0.272—6.02
3. Carbon tetrachloride[a]	Propane-propylene	Carbon tetrachloride	0.337—7.94
4. Perchloroethylene[b]	Propane-propylene	Carbon tetrachloride	0.198—6.99
5. Methyl chloride[b]	Methane	Methylene chloride	0.325—13.68
6. Methylene chloride[b]	Methane	Methylene chloride	0.217—8.86
7. Chloroform[b]	Methane	Methylene chloride	0.230—7.43
8. Carbon tetrachloride[b]	Methane	Methylene chloride	0.235—6.59
9. Carbon tetrachloride	Carbon disulfide	Carbon disulfide	0.027—1.17
10. Propylene oxide (chlorohydrin)	Propylene	Propylene chlorhydrin	0.153—6.22
11. Chlorobenzene	Benzene	Benzene	0.079—1.49
12 Chloroprene	Butadiene	Chloroprene	0.023—1.89
13. Ethyl chloride	Ethanol-ethane	Ethanol	0.127—4.27
14. Methylene chloride	Methanol—methyl chloride	Methylene chloride	0.016—2.33
15. Chloroform	Acetone	Acetone	0.052—1.55
16. Glycerin	Allyl chloride	Allyl chloride	0—0.90
17. Allyl chloride	Propylene	Allyl chloride	0.161—4.81
18. Trichloroethylene	Acetylene	Trichloroethylene	0.037—4.19
19. Benzyl chloride(s)	Toluene	Toluene	0.070—3.30
20. Dichlorophenol	Phenol	Phenol	0.109—2.06
21. Phosgene	Carbon monoxide	None	0.151—2.53
22. Acetyl chloride	Sodium acetate—acetic acid	Acetic acid	0
23. Chloroacetic acid	Acetic acid	Acetic acid	0.094—1.45
24. Hexachlorobenzene	Benzene	Benzene	0.021—1.03

[a] Ranges continued on next page.

[b] Co-products.

Table IV-4. (Continued)

	Organic Carrier Gas		Liquid Organic VOC			Total VOC	
	Flow [scfm/(M lb/yr)]	Emission (lb/M lb)	Concentration[d] (mole fraction)	Flow [scfm/(M lb/yr)]	Emission (lb/M lb)	Flow [scfm/(M lb/yr)]	Emission (lb/M lb)
Product[c]	Min Max	Min Max		Min Max	Min Max	Min Max	Min Max
1.	0.005—1.30	1,600—88,600	0.087	0.005—0.193	770—27,900	0.061—2.21	2,400—117,000
2.	0	0	0.137	0.002—0.084	430—16,400	0.016—0.614	430—16,400
2.	0.175—2.45	16,200—181,000	0.137	0.093—0.956	8,400—186,000	0.315—6.98	24,600—367,000
3.	0.004—1.20	230—10,500	0.127	0.049—1.16	11,000—260,000	0.384—9.10	11,200—271,000
4.	0.003—0.741	200—47,700	0.127	0.029—1.02	6,500—229,000	0.227—8.01	6,700—277,000
5.	0.149—11.1	10,600—527,400	0.493	0.316—13.3	39,300—1,650,000	0.641—27.0	49,900—2,177,000
6.	0.008—5.79	350—254,000	0.493	0.211—8.62	26,200—1,070,000	0.428—17.5	26,600—1,324,000
7.	0.006—4.13	250—181,000	0.493	0.224—7.22	27,800—898,000	0.454—14.7	28,100—1,079,000
8.	0.004—3.19	200—140,000	0.493	0.229—6.41	28,400—797,000	0.464—13.0	28,600—937,000
9.	0	0	0.405	0.018—0.796	2,000—88,500	0.045—1.97	2,000—88,500
10.	0—2.33	0—150,000	0.002	0.0003—0.013	40—1,700	0.153—6.23	40—152,000
11.	0	0	0.105	0.009—0.175	1,100—19,900	0.088—1.67	1,100—19,900
12.	0—0.764	0—62,600	0.040	0.001—0.079	100—10,200	0.024—1.97	100—72,800
13.	0.111—2.11	10,300—143,000	0.062	0.008—0.282	560—19,000	0.135—4.55	10,900—162,000
14.	0.004—0.796	300—59,000	0.493	0.016—2.27	1,900—282,000	0.032—4.60	2,200—341,000
15.	0	0	0.257	0.018—0.536	1,500—45,600	0.070—2.09	1,500—46,600
16.	0	0	0.408	0—0.620	0—69,400	0—1.52	0—69,400
17.	0.045—2.49	2,900—185,000	0.408	0.111—3.32	12,400—371,000	0.272—8.13	15,300—556,000
18.	0.005—2.58	200—106,000	0.082	0.003—0.374	600—71,700	0.040—4.56	800—178,000
19.	0	0	0.031	0.002—0.106	300—14,200	0.072—3.41	300—14,200
20.	0	0	0.003	0.00003—0.0006	4—85	0.109—2.06	4—85
21.	0.108—1.08	10,000—100,000	0	0	0	0.151—2.53	10,000—100,000
22.	0	0	0.016	0	0	0	0
23.	0	0	0.016	0.002—0.024	130—2,100	0.096—1.47	130—2,100
24.	0	0	0.105	0.003—0.121	280—13,800	0.024—1.15	280—13,800

[c] Numbers refer to products listed on preceding page.

[d] Based on pure saturated compound at 21°C and 760 mm Hg.

With the information given here the carrier gases from the various reactions can be estimated. Sample calculations are shown in Appendix D. The total flow from a reaction is equivalent to the carrier-gas flow plus the flow related to VOC from other organic liquids and solids.

B. ESTIMATION OF VOC

The VOC in an organic emission comes from those carrier gases that are organic and from evaporation into the carrier gases of organics that are liquid or solid at ambient conditions. If the equipment design and operation is well known, the partial pressures of the liquid and solid organics present are easily estimated. The maximum VOC concentration would be calculated as the total of the organic liquid or solid partial pressures at the extreme emission conditions (highest ambient temperature and atmospheric pressure). If the gas-liquid (solid) contact surface is small or if the contact time is short, saturation may not be achieved. Prediction of the fraction of saturation requires knowledge of the specific equipment and engineering judgement.

The VOC composition can be estimated as the summation for all the individual components of each component's vapor pressure divided by the total pressure times each component's liquid-phase molar concentration. This sum is then multiplied by the fractional approach to saturation that the system has attained; this product is the estimated VOC composition, y_{VOC}.

The equation for the estimation VOC from organic liquids or solids is shown below:

$$y_{VOC} = A \sum_{i=1}^{n} x_i \frac{p_i^*}{\pi} \qquad \text{(IV-7)}$$

where

y_{VOC} = the mole fraction of organic vapors (VOC) arising from gas contacting liquid or solid organic compounds,

A = the fractional approach to saturation (A = 1 for a saturated vapor),

n = the number of organic compounds present in the liquid or solid,

x_i = the mole fraction of organic component i in the liquid,

P_i^* = the vapor pressure of the ith organic compound at the temperature of the emission,

π = the total pressure (normally atmospheric) at the emission point.

Since we are interested in the range for VOC emissions, y_{VOC} is calculated for the single most volatile liquid present in the chlorination reaction as if it were the only organic present. Saturation is also assumed. Therefore equation IV-7 is simplified to

$$Y_{VOC} = \frac{P_i^* \text{ (mm Hg)}}{760} \quad . \qquad \text{IV-8}$$

Once the VOC concentration from liquids and solids is known, the total flow from the emission and the total VOC content (VOC from carrier gases and from liquids and solids) can be easily calculated.

Table IV-4 gives the carrier-gas flow range, the organic carrier-gas emission, the VOC emission from organic liquids and solids, and the total emission flow range. An example calculation is shown in Appendix D.

C. ACTUAL CHLORINATION REACTION EMISSIONS

Emissions for chlorination reactions reported to the EPA during the IT Enviroscience study are shown in Table IV-5. The information sources are included in Appendix B. The actual data show good agreement with the projections from Table IV-4. The uncontrolled data from Table IV-5 compare with the ranges given in Table IV-4. Many of the real emissions fall at the low end of the ranges predicted. Some of the emission data lie below the minimum values expressed in Table IV-4. These comparisons indicate that assumptions used to develop the emission projections could lead to emission projections higher than realistic ones.

If more sophisticated projections are necessary, further identification or refinement of the factors in Table IV-3 may be necessary. This could be done through a more thorough literature search than was permitted by the available time or funds in this contract or through additional solicitation of industrial data. Better estimates of separation efficiencies could be developed through mass-transfer calculations.

Table IV-5. VOC Emissions from Chlorination Reactors Based on Industry Information

	Total Flow Rate [scfm/($\bar{M}$ lb of product/yr)]			VOC Emissions (lb/$\bar{M}$ lb of product)[b]			
Product	Uncontrolled	Controlled	Emitted	Uncontrolled	Controlled	Emitted	Control Device
Ethylene dichloride	n.r.[a]	0.22	0.22	n.r.	2,280	2,280	Condenser
1,1,1-Trichloroethane	n.r.	0.41	(To incinerator)	n.r.	16,800	(To incinerator)	Condenser (-1°C) then incineration
Ethylene dichloride	n.r.	10.0[c]	10.0[c]	n.r.	n.r.	n.r.	Incineration
Chlorinated methanes	2.57		2.57	28,700		28,700	
Chlorinated methanes	n.r.	n.r.	n.r.	n.r.	n.r.	n.r.	Compressed and condensed
Methyl chloride	n.r.	0.094—0.28	(To flare)	n.r.	7,450—22,400	(To flare)	Condenser (27-33°C); then flared
Propylene oxide	n.r.	n.r.	n.r.	n.r.	10,300	10,300	Absorber (16°C)
Propylene oxide	5.02	n.r.	n.r.	104,200	n.r.	n.r.	Incineration
Chlorobenzene	0.067	0.008	0.008	3,130	88	88	Absorber (30°C)
Chloroprene	n.r.	0.0037	0.0037	n.r.	290	290	Absorber
Allyl chloride	n.r.	n.r.	n.r.	9	n.r.	9	
Trichloroethylene	n.r.	0.031	0.031	n.r.	200	200	Refrigerated condenser

[a] Not reported.

[b] Many VOC emissions estimated by assuming molecular weight of VOC.

[c] Includes combustion gases.

V. CONTROL OPTIONS FOR CHLORINATION REACTORS

The carrier-gas method described in two earlier chapters allows the preliminary selection of control devices that would probably be applicable. Large potential flows, high levels of organic carrier gases, low or high VOC concentrations, and other parameters projected from the carrier-gas method allow rejection of inappropriate control devices without requiring detailed emission information. The following section on add-on controls is an example of how information generated with the carrier-gas method can be used to assess the viability of a control device at a very early stage. One of the potentially applicable control devices has been identified; the best choice can be achieved with the use of cost-effectiveness parameters

The emissions from chlorination reactions range widely from process to process, and it is likely that the control technology for each process will vary. Control for all chlorination reactions include in-process control elements and add-on control devices.

A. IN-PROCESS CONTROL

Clearly, any approach that lowers the amount of carrier gas in the reaction will reduce the emission. This is particularly true of chlorinations that use gaseous organic reactants. In these cases higher organic reactant purities and high chlorine purities may lower the organic emission if the carrier gases from these sources are significant.

Plants incorporating higher separation efficiencies for equipment separating the reaction waste gases will have lower carrier-gas flows and lower organic emissions. High-efficiency chlorine and HCl removal may be significant but often the removal of organic reactants and products is the limiting factor in minimizing the carrier gas. Normally the absorbers used to separate HCl and chlorine are ineffective in removing the unused gaseous organic reactants and products, and separate removal equipment is needed.

Emissions containing large levels of HCl can sometimes be used directly in hydrochlorination reactions at the same plant. This eliminates the chlorination emission but can increase the carrier-gas flow from the hydrochlorination

Table V-1. Possible Add-on Control Devices for VOC Emissions from Chlorination Reactors

			Organic Carrier Gases			Possible Control Technology					
Product	Major Organic Reactant	Most Volatile Liquid Organic	Hydrocarbons	Chlorinated Hydrocarbons	HCl Present	Condensers	Absorbers	Carbon Adsorbers	Flares	Thermal Oxidation	High-Temperature Thermal Oxidation
Ethylene dichloride	Ethylene	Ethylene dichloride	Yes	Yes	No	S^{a}	A^{b}	S^{c}	N^{d}	N^{e}	A
1,1,1-Trichloroethane	Vinyl chloride	1,1,1-Trichloroethane	No	No	No	A^{f}	A^{b}	S^{f}	N^{d}	N^{e}	A
	Ethane	1,1,1-Trichloroethane	Yes	Yes	Yes	S^{a}	$S^{a,b}$	S^{c}	N^{d}	N^{e}	A
Carbon tetrachloride	Propane-propylene	Carbon tetrachloride	Yes	Yes	Yes	A^{f}	$A^{b,f}$	S^{c}	N^{d}	N^{e}	A
Perchloroethylene	Propane-propylene	Carbon tetrachloride									
Carbon tetrachloride	Methane	Methylene chloride	Yes	Yes	Yes	A^{f}	$A^{b,f}$	S^{c}	N^{d}	N^{e}	A
Methylene chloride	Methane	Methylene chloride									
Chloroform	Methane	Methylene chloride									
Methyl chloride	Methane	Methylene chloride									
Carbon tetrachloride	Carbon disulfide	Carbon disulfide	No	No	No	A^{f}	$A^{b,f}$	S^{f}	S^{g}	S^{g}	S
Propylene oxide (chlorohydrin)	Propylene	Propylene chlorohydrin	Yes	No	Yes	S^{a}	A^{b}	S^{c}	N^{d}	S^{g}	S
Chlorobenzene	Benzene	Benzene	No	No	Yes	A^{f}	$A^{b,f}$	S^{f}	N^{d}	S^{g}	S
Chloroprene	Butadiene	Chloroprene	Yes	No	No	A^{a}	A^{b}	S^{c}	S^{g}	A^{f}	S
Ethyl chloride	Ethanol-ethane	Ethanol	Yes	Yes	Yes	S^{a}	$A^{b,f}$	S^{c}	N^{d}	N^{e}	A
Methylene chloride	Methanol—methyl chloride	Methylene chloride	No	Yes	Yes	S^{f}	$A^{b,f}$	S^{f}	N^{d}	N^{e}	A
Chloroform	Acetone	Acetone	No	No	No	A^{f}	A^{f}	S^{f}	S^{g}	S^{g}	S
Glycerin	Allyl chloride	Allyl chloride	No	No	No	A^{f}	A^{f}	S^{f}	S^{g}	S^{g}	S
Allyl chloride	Propylene	Allyl chloride	Yes	Yes	Yes	A^{f}	$A^{b,f}$	S^{f}	N^{d}	S^{g}	S
Trichloroethylene	Acetylene	Trichloroethylene	Yes	No	Yes	$S^{a,b,f}$	$A^{b,f}$	S^{c}	N^{d}	S^{g}	S
Benzyl chloride(s)	Toluene	Toluene	No	No	Yes	A^{f}	$A^{b,f}$	S^{f}	N^{d}	S^{g}	S
Dichlorophenol	Phenol	Phenol	No	No	Yes	A^{f}	A^{f}	S^{f}	N^{d}	S^{g}	S
Phosgene	Carbon monoxide	None	Yes	No	No	N	A^{f}	S^{f}	N^{d}	S^{g}	S
Acetyl chloride	Sodium acetate—acetic acid	Acetic acid	No	No	No	A^{f}	A^{f}	S^{f}	S^{g}	S^{g}	S
Chloracetic acid	Acetic acid	Acetic acid	No	No	Yes	A^{f}	A^{f}	S^{f}	N^{d}	S^{g}	S
Hexachlorobenzene	Benzene	Benzene	No	No	Yes	A^{f}	$A^{b,f}$	S^{f}	N^{d}	S^{g}	S

A = Always, S = Sometimes, N = Never.

[a] Product recovery or pretreatment for other control devices. Will not significantly reduce VOC emission.

[b] Using hydrocarbon solvent.

[c] Low-level VOC concentration. Will not significantly reduce VOC emission.

[d] Noxious gases formed.

[e] High-temperature oxidation required.

[f] Significant VOC reduction possible.

[g] Depending on chlorinated hydrocarbon Cl_2 and HCl level.

reactor. This is not a universal control technique, since all chlorination plants may not manufacture products using HCl.

B. ADD-ON CONTROLS

Since the organic concentrations vary so greatly in chlorination reactions, the choice of an effective control depends on the reaction and the equipment design and operation. However, generalizations can be made by examining the data in Table IV-4. The potential use of add-on controls is summarized in Table V-1. The control device evaluation reports mentioned later are contained in Volumes IV and V.

1. Condensers

Condensers and refrigerated condensers can be used when the concentration of VOC from organic liquids (or solids) is high. VOC resulting from organic carrier gases cannot be removed by condensers. Therefore the overall reduction efficiency in condensers even with high-VOC feeds can be poor. For further information on condensers, consult the condensation control device evaluation report.

2. Absorbers

Absorbers for Cl_2 and HCl recovery have already been included in the carrier-gas calculations. Additional absorbers could be effective on emissions if a solvent with a high affinity for hydrocarbons or chlorinated hydrocarbons is used. One increasingly popular control is the use of a refrigerated liquid to absorb the same liquid and other hydrocarbons from the emission. Further information about the use of absorption as a control technique can be found in the gas absorption control device evaluation report.

3. Adsorption

Because of safety and operating considerations, carbon adsorption may be used for control only if the total VOC concentration is less than about 1 mole %. A few waste gases from chlorination reactors could achieve this requirement if low levels of organic carrier gases, high levels of nonorganic carrier gases, and low-volatility organic liquids are present. Streams can be diluted with air but the cost of control increases to a large extent. Also, carbon has relatively low efficiency for streams whose VOC is composed mostly of organic carrier gases. Further information on carbon adsorption control can be found in the carbon adsorption control device evaluation report.

4. Combustion

Combustion control can be achieved in a wide variety of burners. Flares and fuel gas can be considered only if the percentage of non-chlorine-containing carrier gas is high and that of HCl, chlorine, and chlorinated hydrocarbons is low since the chlorine released in combustion would form noxious flue gases (Cl_2 and HCl). Chlorinated hydrocarbons also have low levels of heat content and therefore are relatively poor fuels. Burners that are not specifically designed to accept chlorine-containing compounds can also suffer severe corrosion problems.

Streams with very low levels of chlorinated hydrocarbons and moderate levels of HCl and nonchlorinated VOC (reactant- or product-related organic carrier gases) can be burned in low-temperature thermal oxidizers equipped for removal of halogen from the flue gas. Streams with high levels of chlorinated hydrocarbons and moderate to high levels of HCl and chlorine can be controlled with high-temperature thermal oxidizers equipped for removal of halogen from the flue gas. Further information on these control technologies can be found in the following control device evaluations reports:

1. Flares and the Use of Emissions as Fuels
2. Thermal Oxidation
3. Thermal Oxidation Supplement (VOC Containing Halogens or Sulfur)

Catalytic oxidation is normally not acceptable since the chlorine in the waste gas can poison the catalyst. Further information on catalytic oxidation can be found in the catalytic oxidation control device evaluation report.

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APPENDIX A

PRODUCTS ORGANIZED BY UNIT PROCESSES

Table A-1. Products Organized by Unit Processes

Product	Process
Acidification Reactions	
22.[a] Phenol	3% Chlorobenzene
22. Phenol	2% Benzene sulfonation
99. Salicylic acid	100% Sodium phenate
Addition Esterification Reactions	
35. Vinyl acetate (VA)	13% Acetylene vapor phase
Alcoholysis Reactions	
68. Glycol ethers	97% Ethylene oxide
68. Glycol ethers	3% Propylene oxide
95. *n*,*n*-Dimethyl aniline	100% Aniline alcoholysis
Alkylation Reactions	
8. Ethylbenzene	98% Benzene alkylation
20. Cumene	100% Benzene
31. Alkyl leads	95% Ethyl chloride
51. Nonyl phenol	100% Phenol alkylation
71. Linear alkyl benzene	100% Benzene alkylation
74. Methyl styrene	85% Cumene process by-product
94. Cresylic acids (SYN)	8% Phenol/methanol
116. Benzophenone	100% Benzene/carbon tetrachloride
Ammonolysis Reactions	
34. Ethanolamines	100% Ethylene oxide
58. Adiponitrile/HMDA	24% Adipic acid
61. Pyridine	100% Formaldehyde/acetaldehyde
75. Ethylene diamine/triethylene tetramine	100% EDC ammonolysis
108. Mono-, di-, trimethyl amines	100% Methanol ammonolysis
114. Mono-, di-, triethyl amine	100% Ethanol ammonolysis
119. Butyl amines	100% Butyraldehyde hydrogenation
121. Propyl amines (M-D-T)	50% *n*-Propyl chloride
121. Propyl amines (M-D-T)	50% *n*-Propyl alcohol
136. Amino ethylethanolamine	100% Ethylene oxide
137. Cyclohexylamines	50% Cyclohexanone

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[a] Refers to rank-order number in Table II-1.

Table A-1. (Continued)

Product	Process
Ammoxidation Reactions	
2. Acrylonitrile	100% Propylene oxidation
9. Hydrogen cyanide (HCN)	50% Andrussow process
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product
Bromination Reactions	
89. Ethylene dibromide	100% Ethylene bromination
117. Methyl bromide	100% Methanol/HBR and bromine
Carbonylation Reactions	
28. Acrylic acid	23% Modified Reppe
29. Acetic acid	19% Methanol
76. Ethyl acrylate	61% Acetylene (Reppe)
99. Salicylic acid	100% Sodium phenate
Cleaving Reactions	
107. Hydroquinone	100% Acetone co-product
Chlorination Reactions	
3. Ethylene dichloride	50% Direct chlorination
11. 1,1,-Trichloroethane	74% Vinyl chloride
11. 1,1,-Trichloroethane	10% Ethane chlorination
12. Carbon tetrachloride	42% Chloroparaffin chlorinolysis
12. Carbon tetrachloride	20% Methane
12. Carbon tetrachloride	38% Carbon disulfide
15. Propylene oxide	60% Chlorohydrin
25. Perchloroethylene	34% Ethane chlorinolysis
25. Perchloroethylene	66% Ethylene dichloride
27. Chlorobenzene	100% Benzene chlorination
30. Chloroprene	100% Via butadiene
33. Ethyl chloride	44% Ethanol/ethane
36. Methylene chloride	65% Methanol/methyl chloride
36. Methylene chloride	35% Methane chlorination
40. Chloroform	39% Methanol chlorination
40. Chloroform	61% Methane chlorination
44. Glycerol (synthetic only)	71% Epichlorohydrin
57. Allyl chloride	100% Propylene chlorination
59. Trichloroethylene	9% Acetylene

Table A-1. (Continued)

Product	Process
59. Trichloroethylene	91% Ethylene dichloride
77. Methyl chloride	2% Methane chlorination
91. Benzyl chloride	100% Toluene chlorination
92. Dichlorophenol	45% Phenol chlorination
97. Phosgene	100% Carbon monoxide/chlorine
98. i-Butanol	79% Propylene oxide co-product
113. Acetyl chloride	100% Sodium acetate
115. Chloroacetic acid	100% Acetic acid chlorination
132. Hexachlorobenzene	100% Hexachlorocyclohexane
140. Benzoyl chloride	100% Benzoic acid
Condensation Reactions	
15. Propylene oxide	40% Peroxidation
47. Bisphenol A	100% Phenol/acetone
50. Pentaerythritol	100% Formaldehyde/acetaldehyde
60. Methyl isobutyl ketone (MIBK)	100% Acetone
64. Urea	100% Ammonia/carbon dioxide
73. Diphenylamine	100% Aniline amination
85. 2-Ethyl 1-hexanol	100% Condensation
86. n-Butanol (butyl alcohol)	20% Acetaldehyde
131. Cyclooctadiene	100% Butadiene dimerization
Dehydration Reactions	
64. Urea	100% Ammonia/carbon dioxide
85. 2-Ethyl 1-hexanol	100% Condensation
20. Ethyl (diethyl) ether	100% Ethanol
22. Crotonaldehyde	100% Aldo process
28. Allyl alcohol	6% Propylene glycol dehydration
Dehydrochlorination Reactions	
1. Vinyl chloride	99% Ethylene dichloride
30. Chloroprene	100% Via butadiene
38. Vinylidene chloride	50% 1,1,2-Trichloroethylene
38. Vinylidene chloride	50% 1,1,-Trichloroethylene
44. Glycerol (synthetic only)	71% Epichlorohydrin
60. Methyl isobutyl ketone (MIBK)	100% Acetone
92. Dichlorophenol	55% Trichlorobenzene

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Table A-1. (Continued)

Product	Process
Dehydrogenation Reactions	
10. Styrene	100% Ethyl benzene
32. Acetone	31% Isopropanol
66. Isoprene	33% Isoamylene extraction
74. Methyl styrene	15% Cumene dehydrogenation
105. Methyl ethyl ketone (MEK)	75% sec-Butanol
132. Hexachlorobenzene	100% Hexachlorocyclohexane
Esterification Reactions	
6. Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid
6. Dimethyl terephthalate (DMT)	25% Hercules
6. Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid
6. Dimethyl terephthalate (DMT)	35% Du Pont
14. Methyl methacrylate (MMA)	100% Acetone cyanohydrin
49. Cellulose acetate	100% Cellulose esterification
76. Ethyl acrylate	39% Direct esterification
84. Diisooctyl phthalate (di-2-ethylhexyl)	100% Phthalic anhydride/alcohol
88. Ethyl acetate	100% Acetic acid
102. Diisoldcyl phthalate	100% Phthalic anhydride/isodecanol
103. Butyl acrylate	100% Acrylic acid esterification
125. Ethylene glycol methyl ethyl ether acetate	100% Ethoxy ethanol ester
129. Isopropyl acetate	100% Isopropanol esterification
130. Methyl acetate	100% Acetic acid/methanol
133. *n*-Butyl acetate	100% Esterification
139. Benzyl benzoate	50% Benzaldehyde
139. Benzyl benzoate	50% Benzyl alcohol/acid
Fluoronation Reactions	
24. Fluorocarbons	100% CCl_4/C_2Cl_6 fluorination
Fusion Reactions	
22. Phenol	2% Benzene sulfonation
94. Cresylic acids (syn)	8% Toluene sulfonation

Table A-1. (Continued)

	Product	Process
	Hydration Reactions	
18.	Ethylene glycol	100% Ethylene oxide
42.	Isopropanol (isopropyl alcohol)	100% Propylene/sulfuric acid
44.	Glycerol (synthetic only)	71% Epichlorohydrin
44.	Glycerol (synthetic only)	15% Allyl alcohol
44.	Glycerol (synthetic only)	14% Acrolein
53.	Diethylene, triethylene glycols	100% Co-products w/ethylene glycol
55.	Propylene glycols (mono- di- tri-)	100% Propylene oxide hydration
63.	Ethanol (ethyl alcohol)	100% Ethylene
70.	sec-Butanol	100% Butylenes
96.	Acetylene	30% Calcium carbide
	Hydrocyanation Reactions	
58.	Adiponitrile/HMDA	65% Butadiene
90.	Acetone cyanolhydrin	100% Acetone cyanation
119.	Butyl amines	100% Butyraldehyde hydrogenation
121.	Propyl amines (M-D-T)	50% n-Propyl alcohol
	Hydrochlorination Reactions	
11.	1,1,1-Trichloroethane	74% Vinyl chloride
11.	1,1,1-Trichloroethane	16% Vinylidene chloride
33.	Ethyl chloride	96% Ethylene chlorination
77.	Methyl chloride	98% Methanol hydrochlorination
104.	Chlorosulfonic acid	100% SO_3 hydrochlorination
	Hydrodealkylation	
62.	Benzene	20% Toluene hydrodealkylation
79.	n-Butyraldehyde	100% Oxo process
112.	Biphenyl	100% Toluene hydrodealkylation
	Hydrodimerization Reactions	
58.	Adiponitrile/HMDA	11% Acrylonitrile
	Hydroformylation Reactions	
86.	n-Butanol (butyl alcohol)	80% Oxo process
87.	Propionic acid	93% Oxo process
93.	Isobutyraldehyde	100% Oxo process
106.	Isobutanol (isobutyl alcohol)	100% Oxo process

Table A-1. (Continued)

	Product	Process
	Hydroformylation Reactions (Continued)	
118.	Propyl alcohol	87% Oxo process
123.	Isooctyl alcohol	100% Oxo process/hydrogenation
127.	Isodecanol	75% Oxo process
	Hydrogenation Reactions	
19.	Cyclohexanol/cyclohexanone	25% Phenol
23.	Aniline	100% Nitrobenzene hydrogenation
44.	Glycerol (synthetic only)	14% Acrolein
46.	Cyclohexane	84% Benzene hydrogenation
58.	Adiponitrile/HMDA	65% Butadiene
60.	Methyl isobutyl ketone (MIBK)	100% Acetone
63.	Ethanol (ethyl alcohol)	100% Ethylene
85.	2-Ethyl 1-hexanol	100% Condensation
86.	n-Butanol (butyl alcohol)	20% Acetaldehyde
119.	Butyl amines	100% Butyraldehyde hydrogenation
137.	Cyclohexylamine	50% Aniline
	Hydrolysis Reactions	
14.	Methyl methacrylate (MMA)	100% Acetone cyanohydrin
22.	Phenol	3% Chlorobenzene
52.	Acrylamide	100% Acrylonitrile
56.	Epichlorohydrin	100% Allyl chloride/HCL
67.	Furfural	100% Polysaccharides hydrolysis
116.	Benzophenone	100% Benzene/carbon tetrachloride
128.	Allyl alcohol	47% Allyl chloride hydrolysis
135.	Dinitrophenol	100% Dinitration of phenol
	Isomerization Reactions	
30.	Chloroprene	100% Via butadiene
49.	Caprolactam	100% Cyclohexanone
54.	Fumaric acid	100% Maleic acid/isomerization
128.	Allyl alcohol	47% Propylene oxide isomerization
	Neutralization Reactions	
22.	Phenol	2% Benzene sulfonation
49.	Caprolactam	100% Cyclohexanone
98.	t-Butanol	21% Isobutylene

Table A-1. (Continued)

Product	Process
Nitration Reactions	
17. Nitrobenzene	100% Benzene nitration
45. Nitrophenol	100% Phenol nitration
69. Dinitrotoluene	100% Toluene dinitration
80. Nitroaniline	100% Nitro chlorobenzene
110. Chloronitrobenzene	100% Chlorobenzene nitration
Oxidation Reactions	
4. Maleic anhydride	85% Benzene oxidation
4. Maleic anhydride	15% Butane oxidation
5. Ethylene oxide	34% O_2 oxidation/ethylene
5. Ethylene oxide	66% Air oxidation/ethylene
6. Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid
6. Dimethyl terephthalate (DMT)	25% Hercules
6. Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid
6. Dimethyl terephthalate (DMT)	35% Du Pont
13. Formaldehyde	23% Metal oxide/methanol
13. Formaldehyde	77% Silver catalyst/methanol
19. Cyclohexanol/cyclohexanone	75% Cyclohexane
22. Phenol	2% Toluene oxidation
22. Phenol	93% Cumene
26. Terephthalic acid (TPA)	39% Amoco
26. Terephthalic acid (TPA)	14% Mobil
26. Terephthalic acid (TPA)	47% Eastman
28. Acrylic acid	77% Propylene oxidation
29. Acetic acid	33% Acetaldehyde
29. Acetic acid	44% Butane oxidation
32. Acetone	31% Isopropanol
32. Acetone	69% Cumene
41. Phthalic anhydride	70% o-Xylene
41. Phthalic anydride	30% Naphthalene
43. Acetic anhydride	100% Acetic acid
65. Acetaldehyde	100% Ethylene
72. Acrolein	100% Propylene oxidation

Table A-1. (Continued)

Product	Process
Oxidation Reactions	
81. Acetophenone	40% Ethyl benzene oxidation
82. Isophthalic acid	100% m-Xylene oxidation
83. Benzoic acid	100% Toluene air oxidation
94. Cresylic acids (syn)	4% Cumene oxidation
•• •96. Acetylene	62% Hydrocarbon oxidation
100. Dimethyl hydrazine	100% Nitrosodimethyl amine
105. Methyl ethyl ketone (MEK)	25% Butane oxidation
107. Hydroquinone	100% Acetone co-product
109. Adipic acid	100% Cyclohexane
111. Carbon disulfide	100% Methane/sulfur vapor
118. Propyl alcohol	13% Propane oxidation
124. Formic acid	98% n-Butane oxidation
127. Isodecanol	25% n-Paraffin oxidation
134. Butyric acid	33% Butyraldehyde oxidation
134. Butyric acid	67% n-Butane oxidation
139. Benzyl benzoate	50% Benzaldehyde
Oximation Reactions	
49. Caprolactam	100% Cyclohexanone
Oxyacetylation Reactions	
35. Vinyl acetate (VA)	72% Ethylene vapor phase
35. Vinyl acetate (VA)	15% Ethylene liquid phase
Oxychlorination Reactions	
1. Vinyl chloride	1% Acetylene
3. Ethylene dichloride	50% Oxychlorination
Peroxidation Reactions	
15. Propylene oxide	40% Peroxidation
44. Glycerol (synthetic only)	15% Allyl alcohol
44. Glycerol (synthetic only)	14% Acrolein
59. Trichloroethylene	91% Ethylene dichloride
81. Acetophenone	60% Cumene peroxidation
Phosgenation Reactions	
39. Toluene diisocyanate (TDI)	100% Diaminotoluene
78. Methylene diphenylene diisocyanate	100% DPMDA/phosgene

Table A-1. (Continued)

	Product	Process
	Pyrolysis (Chlorinolysis) Reactions	
7.	Ethylene	46% Naphtha/gas-oil pyrolysis
7.	Ethylene	52% Natural-gas liquids pyrolysis
12.	Carbon tetrachloride	42% Chloroparaffin chlorinolysis
16.	Propylene	16% Natural-gas liquids pyrolysis
16.	Propylene	54% Naphtha/gas-oil pyrolysis
21.	Methanol (methyl alcohol)	100% Methane
25.	Perchloroethylene	34% Ethane chlorinolysis
37.	1,3-Butadiene	13% *n*-Butane
37.	1,3-Butadiene	80% Ethylene co-product
37.	1,3-Butadiene	7% *n*-Butene
	Reforming Reactions	
21.	Methanol (methyl alcohol)	100% Methane
	Reduction Reactions	
31.	Alkyl leads	5% Electrolysis
139.	Benzyl benzoate	50% Benzaldehyde
	Saponification Reactions	
15.	Propylene oxide	60% Chlorohydrin
98.	*i*-Butanol	79% Propylene oxide co-product
122.	Crotonaldehyde	100% Aldo process
	Sulfonation Reactions	
22.	Phenol	2% Benzene sulfonation
42.	Isopropanol (isopropyl alcohol)	100% Propylene/sulfuric acid
70.	sec-Butanol	100% Butylens
94.	Cresylic acids (SYN)	8% Toluene sulfonation
104.	Chlorosulfonic acid	100% SO_3 hydrochlorination
126.	Linear alkyl benzene sulfonate	100% Lab sulfonation
138.	Toluene sulfonic acids	100% Toluene sulfonation
	Separations	
7.	Ethylene	22% Refinery by-product
8.	Ethylbenzene	2% Mixed xylene extract
16.	Propylene	30% Refinery by-product

Table A-1. (Continued)

Product	Process
	Separations (Continued)
46. Cyclohexane	16% Petroleum distillation
62. Benzene	80% Not in project scope
66. Isoprene	67% C_4 hydrocarbons
94. Cresylic acids (SYN)	80% Natural coal tar
96. Acetylene	8% Ethylene by-product
98. *i*-Butanol	21% Isobutylene
101. Dodecene	100% Nonene co-product

APPENDIX B

EPA INFORMATION SOURCES

Trip Reports Surveyed for the Organic Emission Data Base

1. Acetaldehyde

    Texas Eastman
    Celanese Chemical Co.

2. Acetic Acid

    Monsanto Chemical Co.
    Borden, Inc.
    Union Carbide Corp.

3. Acetic Anhydride

    Celanese Chemical Co.
    Tennessee Eastman Co.

4. Acrolein-Glycerin

    Shell Oil Co.
    Dupont
    Vistron Corp.

5. Acrylic Acid and Acrylate Esters

    Union Carbide Corp.
    Rohm & Haas Co.

6. Allyl Chloride—Epichlorohydrin

    Shell Oil Co.

7. C_2 Chlorinated Hydrocarbon

    Dow Chemical

8. Chlorobenzenes

    Monsanto Chemical Co.
    PPG Industries

9. Chloromethanes

    Vulcan Materials Co.

10. Cyclohexane

    Phillips Puerto Rico Core, Inc.
    Exxon Chemical Co.

11. Cyclohexanol/Cyclohexanone and Caprolactam

    Nipro, Inc.
    Allied Chemical
    Monsanto Textiles Co.

12. Dimethyl Terephthalate

    Hercofina Hanover

13. Ethyl Acetate

    Celanese Chemical Co.

14. Ethylbenzene and Styrene

    Dow Chemical Co.
    Cosden Oil & Chemical Co.

15. Ethylene and Butadiene/1591 and 1592 Olefin Processes

    Arco Chemical Co.
    Petro-Tex Chemical Corp.
    Gulf Oil Chemical Co.

16. Ethylene Dichloride

    Dow Chemical Co.
    Borden Chemical Co. - Stauffer

17. Ethylene Oxide

    BASF Wyandotte Corp.
    Celanese Chemical Co.
    Union Carbide Corp.

18. Fluorocarbons

    Allied Chemical Co.

19. Formaldehyde

    Celanese Chemical Co.
    Borden, Inc.

20. Glycol Ethers

    Union Carbide
    Dow Chemical Co.

21. Linear Alkylbenzene

    Union Carbide Corp.
    Monsanto Co.

22. Maleic Anhydride

Amoco Corp.
Denka Chemical Corp.
Monsanto Chemical Co.
Reichhold Chemicals, Inc.

23. Methanol

Borden, Inc.
Celanese Chemical Co.
Monsanto Co.

24. Methyl Methacrylate

Rohm & Haas
Dupont

25. Nitrobenzene/Aniline

Du Pont
Rubicon Chemical

26. Phenol/Acetone

Monsanto Chemical Co.

27. Propylene Oxide

Dow Chemical Co.
Oxirane Chemical Co.

28. Terephthalic Acid

Amoco Chemical Corp. - Standard

29. Toluene Diisocyanate

Allied Chemical Co.

30. Vinyl Acetate

Celanese Chemical Co.
Union Carbide Corp.

31. Waste Acid Recovery (Sulfuric Acid)

Dupont

Letter Responses to EPA Requests for Information

1. Acetic Acid

Tennessee Eastman Co., Kingsport, TN	J. C. Edwards	5/15/78

2. Acetone

Tennessee Eastman Co., Kingsport, TN	J. C. Edwards	9/25/78
Exxon Chemical Company USA, Bayway Chemical Plant, NJ	C. R. Ball	10/13/78
Shell Oil Co., Houston, TX	J. A. Mullins	10/25/78
Union Carbide Corp., Cumene at Ponce, Puerto Rico	F. D. Bess	9/21/78

3. Acrolein

Union Carbide Corp., Taft, LA	F. D. Bess	4/21/78

4. Acrylic Acid and Esters

Celanese Chemical Co., Inc., Clear Lake plant, TX	C. R. DeRose	4/21/78

5. Adipic Acid

E. I. du Pont de Nemours & Co., Victoria, TX	D. W. Smith	4/20/78
E. I. du Pont de Nemours & Co., Orange, TX	D. W. Smith	9/28/78
Mobay Chemical Corp., Pittsburgh, PA	Lee P. Hughes	1/31/78

6. Adiponitrile—Hexamethylenediamine

E. I. du Pont de Nemours & Co., Orange, TX, Sabine River Works and Victoria plant	J. R. Cooper	2/9/79
Celanese Chemical Co., Inc., Bay City, TX	R. H. Maurer	10/3/78
Monsanto Co., Pensacola, FL	F. T. Osborne	10/27/78

7. Aniline

E. I. du Pone de Nemours & Co., Gibbstown, NJ	D. W. Smith	2/3/78

8. Carbon Tetrachloride

E. I. du Pont de Nemours & Co., Corpus Christi, TX	D. W. Smith	3/23/78

9. Catalytic Oxidation

Diamond Shamrock, Cleveland, OH	W. R. Taylor	10/3/77
Notes on meeting, EPA, Durham NC	J. A. Key	8/23/79
Rhone-Poulenc S.A., Neuilly-sur-Seine	J. C. Zimmer	5/29/79

10. Chlorinated Methanes - Methyl Chloride

General Electric Co., Waterford, NY	R. L. Hatch	8/8/78
Allied Chemical, Moundsville, WV	J. V. Muthig	3/31/78
Union Carbide Corp.	F. D. Bess	8/3/78
Ethyl Corp., Baton Rouge, LA	W. C. Strader	8/2/78
Diamond Shamrock, Belle, WV	S. G. Lant	4/3/78
E. I. du Pont de Nemours & Co., Niagara Falls, NY	D. W. Smith	3/23/79
Dow Chemical USA, Texas Division	J. Beale	4/28/78

11. Chlorobenzene

Dow Chemical USA, Michigan Division	J. Beale	3/14/78
Montrose Chemical Corp. of California, Henderson, NV	H. J. Wurzer	3/7/78

12. Chloroprene

Denka Chemical Corp., Houston, TX	A. J. Meyer	3/26/79
Petro-Tex Chemical Corp. (sold to Denka)		
E. I. du Pont de Nemours & Co., La Place, LA	H. A. Smith	11/28/78

13. Cyclohexanol/Cyclohexanone

Union Carbide Corp., Taft, LA	F. D. Bess	5/5/78
Celanese Chemical Co., Inc., Bay City, TX	C. J. Schaefer	4/21/78

14. Cyclohexane

CORCO Cyclohexane, Inc.		1/24/78
Cosden Oil & Chemical Co., Big Spring, TX	Bob Fuller	1/24/78
Champlin Petroleum Co., Corpus Christi, TX	R. L. Chaffin	1/25/78
Sun Petroleum Products Co., Tulsa, OK	W. W. Dickinson	1/26/78
Gulf Oil Company, Port Arthur, TX	M. P. Zanotti	1/26/78

15. Cumene

Ashland Petroleum Co., Catlettsburg, KY	O. J. Zandona	9/25/78
Sun Petroleum Products Co., Corpus Christi, TX	J. R. Kampfhenkel	9/12/78
Gulf Oil Company, Port Arthur, TX	M. P. Zanotti	9/19/78
Shell Oil Company, Deer Park, TX		
Monsanto Chemical Intermediates Co., Alvin, TX	M. A. Pierle	

16. Chlorinated C_2-Methyl Chloroform, Perchloroethylene, Trichloroethylene, Trichloroethane

Dow Chemical USA, Freeport, TX	F. E. Homan	1/20/78
Ethyl Corporation, Baton Rouge, LA	W. C. Strader	11/28/78
Dow Chemical USA, Louisiana Division	J. S. Beale	12/5/78
PPG Industries, Inc., Lake Charles, LA	F. C. Dehn	3/14/79
Vulcan Materials Co., Geismar, LA	T. A. Leonard	3/8/79

17. Dimethyl Terphthalate/Terephthalic Acid

Tennessee Eastman Co., Kingsport, TN	J. C. Edwards	8/31/78
Hoechst Fibers Industries, Spartanburg, SC	R. M. Browning	8/14/78
Amoco Chemicals Corp., Joliet, IL	H. M. Brennan	8/16/78
E. I. du Pont de Nemours & Co., Cape Fear, NC, and Old Hickory, TN	D. W. Smith	10/20/78

18. Ethanolamines

Dow Chemical USA, Plaquemine, LA	J. S. Beale	9/15/78
Texaco Petrochemicals, Port Neches, TX	J. F. Cooper	2/9/79
Olin Chemicals, Brandenburg, KY	L. B. Anziano	5/17/78

19. Ethyl Acetate

Tennessee Eastman Co., Kingsport, TN	J. C. Edwards	8/11/78
Monsanto, Trenton, MI, Springfield, MA	N. B. Galluzzo	
Texas Eastman Co., Longview, TX	G. Prendergast	1/26/79

20. Ethylene

Texas Eastman Co., Longview, TX	G. Prendergast	2/21/78
Exxon Chemical Co. USA, Baton Rouge, LA	J. P. Walsh	2/10/78
Phillips Petroleum Co., Sweeny, TX	L. A. McReynolds	1/27/78
Shell Oil Co., Deer Park, TX	A. G. Smith	2/22/78

21. Ethylene Dichloride

Allied Chemical, Baton Rouge, LA	W. M. Reiter	4/18/75
B. F. Goodrich Chemical Co., Calvert City, OH	W. C. Holbrook	4/7/75
Conoco Chemicals, Lake Charles, LA	J. A. DeBernardi	5/16/78
PPG Industries, Lake Charles, LA	R. J. Samelson	6/2/78
PPG Industries, Lake Charles, LA	F. C. Dehn	4/15/75
PPG Industries, Lake Charles, LA	A. T. Taetzsch	6/21/74
Shell Oil Co., Norco, LA, Deer Park, TX	R. E. VanIngen	4/10/75
Vulcan Materials, Co., Geismar, LA		4/23/75

22. Ethylene Glycol

Calcasieu Chemical Corp., Lake Charles, LA	P. M. Ableson	12/20/78
Shell Oil Co., Geismar, LA	J. A. Mullins	1/11/79
BASF Wyandotte Corp., Geismar, LA	T. R. Kovacevich	11/27/78

23. Ethylbenzene-Styrene

American Hoechst Corp., Baton Rouge, LA	L. T. Bufkin	1/26/78
Atlantic-Richfield Co., Port Arthur, TX, and Beaver Valley, PA	W. G. Kelly	2/23/78
El Paso Products Co., Odessa, TX	C. R. Kuykendall	1/31/78
Gulf Oil Chemicals Co., St. James, LA	F. E. Berry	1/27/78
Monsanto Chemical, Texas City, TX	H. M. Keating	4/28/78
Union Carbide Corp., TX, and Puerto Rico	F. D. Bess	5/5/77
Sun Oil Co. of PA, Corpus Christi, TX		

24. Flares

Exxon Chemical Co. USA, Bayway, NJ	R. R. Schirripa	5/1/79
Dow Chemical USA	S. L. Arnold	5/15/79
Shell Oil Co., Houston, TX	J. A. Mullins	4/12/79
Phillips Petroleum Co., Bartlesville, OK	J. J. Moon	5/4/79
Allied Chemical	E. J. Shields	4/30/79
Gulf Oil Chemicals Co., St. James, LA	F. E. Berry	8/17/78

25. Fluorocarbon

E. I. du Pont de Nemours & Co., Louisville, KY	D. W. Smith	8/21/78
E. I. du Pont de Nemours & Co., Deepwater, NJ	D. W. Smith	6/7/78

26. Formaldehyde

Georgia Pacific Corp., Lufkin, TX	V. J. Tretter, Jr.	7/19/78
Reichhold Chemicals, Inc., Moncure, NC	P. S. Hewett	7/21/78

27. Formic Acid

Rockland Industries, Inc., Middlesboro, MA	Mrs. C. Glass	9/18/78
Sonoco Products Co., Hartsville, SC	C. N. Betts	10/10/78

28. Fugitive

Monsanto Textiles Co., Pensacola, FL	J. J. Vick	8/3/78

29. Glycerine

FMC Corporation, Bayport, TX	C. B. Hopkins	2/6/79

30. Linear Alkylbenzene

Witco Chemical, Wilmington, CA	E. A. Vistica	2/6/78
Conoco Chemicals, Baltimore, MD	D. J. Lorine	2/17/78

31. Maleic Anhydride

Monsanto Chemical, St. Louis, MO	M. A. Pierle	3/22/78

32. Fumaric Acid

Pfizer Inc., Vigo plant, Terre Haute, IN	T. W. Cundiff	4/16/79
Hooker, Puerto Rico	L. F. Wood, Jr.	2/9/79

33. Methanol/Methyl Ethyl Ketone

IMC Chemical Group, Inc., Sterlington, LA	R. E. Jones, Jr.	4/26/78
Rohm and Haas Texas Inc., Deer Park, TX	D. A. Copeland	5/19/78
E. I. du Pont de Nemours & Co., Beaumont, TX	D. W. Smith	5/25/78

34. Methyl Methacrylate

CY/RO Industries, Avondale, LA	D. H. Gold	5/4/78
Texas Air Control Board	C. R. Barden	11/7/72
Exxon Chemical Co. USA, Bayway, TX	B. L. Taranto	6/7/78
ARCO Chemical, Lyondell plant	C. N. Hudson	5/15/78
Shell Oil Co., Martinez plant	J. A. Mullins	5/1/78
Shell Oil Co., Deer Park, TX	J. A. Mullins	6/22/78

35. Nitrobenzene-Aniline

U.S.E.P.A. First Chemical Corp., Pascagoula, MS	D. A. Beck	2/3/78

36. Olefins

Mobil Chemical Co., Beaumont, TX	P. B. Mullin	1/26/78

37. Toluene Diisocyanate

Union Carbide Corp., Charleston, WV, plant	J. C. Ketcham	5/16/78

38. Vinylidene Chloride

Dow Chemical USA, Plaquemine, LA	J. Beale	10/25/78

39. Vinyl Acetate

E. I. du Pont de Nemours & Co., Houston, TX	D. W. Smith	9/18/78
National Starch & Chemical Corp., Long Mott, TX	E. W. Bousquet	8/22/78
U.S. Industrial Chemicals Co., Deer Park, TX	K. G. Carpenter	8/17/78
Celanese Chemical Co., Clear Lake, TX	C. R. DeRose	8/14/78

40. Waste Acid Recovery (Sulfuric Acid)

Celanese Chemical Co., Inc., Corpus Christi, TX	J. M. Mullins	3/29/79
Texas Eastman Co., Longview, TX	G. Prendergast	4/17/79
Colgate-Palmolive Co., Berkeley, CA	T. M. Casey	4/16/79
Amoco Chemicals Corp., Texas City, TX	H. M. Brennan	4/2/79
Allied Chemical, Richmond, CA	W. M. Reiter	5/8/79
Stauffer Chemical Co., Baytown, TX	J. W. Call	8/6/79
Purex Corporation, Edgewater, NJ	K. E. Blackwell	3/28/79
Shell Oil Co., Deer Park, TX	J. A. Mullins	5/4/79
Mobay Chemical Corp., Baytown, TX	L. P. Hughes	4/10/79
Exxon Chemical Co., Baton Rouge, LA	J. P. Walsh	4/27/79
ARCO Chemical Co., Lyondell plant	C. N. Hudson	4/30/79
Exxon Chemical Co., Baton Rouge, LA	J. P. Walsh	4/27/79
ARCO Chemical Co., Lyondell plant	C. N. Hudson	4/30/79
Olin Chemicals Group, Beaumont, TX	H. T. Emerson	5/14/79

APPENDIX C

PRODUCTS ORGANIZED BY CARRIER GASES

Table C-1. Various Reactant Carrier Gases[a]

Product	Process	Carrier Gas
	1-Carbon-Atom Reactants	
7.[b] Ethylene	46% Naphtha/gas-oil pyrolysis	Methane
7. Ethylene	2% Refinery by-product	Methane
7. Ethylene	52% Natural-gas liquids pyrolysis	Methane
9. Hydrogen cyanide (HCN)	50% Andrussow process	Methane
12. Carbon tetrachloride	20% Methane	Methane
16. Propylene	54% Naphtha/gas-oil pyrolysis	Methane
16. Propylene	16% Natural-gas liquids pyrolysis	Methane
16. Propylene	30% Refinery by-product	Methane
21. Methanol (methyl alcohol)	100% Methane	Methane
31. Alkyl leads	5% Electrolysis	Methyl chloride
36. Methylene chloride	35% Methane chlorination	Methane
36. Methylene chloride	65% Methanol/methyl chloride	Methyl chloride
37. 1,3-Butadiene	80% Ethylene co-product	Methane
40. Chloroform	61% Methane chlorination	Methane
50. Pentaerythritol	100% Formaldehyde/acetaldehyde	Formaldehyde
58. Adiponitrile/HMDA	65% Butadiene	Hydrogen cyanide
61. Pyridine	100% Formaldehyde/acetaldehyde	Formaldehyde
77. Methyl chloride	2% Methane chlorination	Methane
90. Acetone cyanyohyrin	100% Acetone cyanation	Hydrogen cyanide
96. Acetylene	62% Hydrocarbon oxidation	Methane
96. Acetylene	8% Ethylene by-product	Methane
111. Carbon disulfide	100% Methane/sulfur vapor	Methane
119. Butyl amines	100% Butraldehyde hydrogenation	Hydrogen cyanide
	2-Carbon-Atom Reactants	
3.[b] Ethylene dichloride	50% Direct chlorination	Ethane, ethylene
3. Ethylene dichloride	50% Oxychlorination	Ethane, ethylene
5. Ethylene oxide	34% O_2 oxidation/ethylene	Ethane, ethylene
5. Ethylene oxide	66% Air oxidation/ethylene	Ethane, ethylene
7. Ethylene	2% Refinery by-product	Ethane, ethylene
7. Ethylene	46% Naptha/gas oil pyrolysis	Ethane, ethylene
7. Ethylene	52% Natural-gas liquids pyrolysis	Ethane, ethylene
8. Ethylbenzene	98% Benzene alkylation	Ethyl chloride
11. 1,1,1-Trichloroethane	10% Ethane chlorination	Ethane

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[a] See Table III-3.

[b] Refers to rank-order number in Table III-3.

Table C-1. (Continued)

Product	Process	Carrier Gas
3-Carbon-Atom Reactants		
1.[b] Vinyl chloride	1% Acetylene	Propylene, propyne
2. Acrylonitrile	100% Propylene oxidation	Propane, propylene
7. Ethylene	2% Refinery by-product	Propane, propylene
7. Ethylene	52% Natural-gas liquids pyrolysis	Propane, propylene
7. Ethylene	46% Naphtha/gas-oil pyrolysis	Propane, propylene
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	Propane, propylene
12. Carbon tetrachloride	42% Chloroparaffin chlorinolysis	Propane, propylene
15. Propylene oxide	40% Peroxidation	Propane, propylene
15. Propylene oxide	60% Chlorohydrin	Propane, propylene
16. Propylene	30% Refinery by-product	Propane, propylene
16. Propylene	54% Naphtha/gas-oil pyrolysis	Propane, propylene
16. Propylene	16% Natural-gas liquids pyrolysis	Propane, propylene
28. Acrylic acid	77% Propylene oxidation	Propane, propylene
37. 1,3-Butadiene	80% Ethylene co-product	Propane, propylene
42. Isopropanol (isopropyl alcohol)	100% Propylene/sulfuric acid	Propane, propylene
44. Glycerol (synthetic only)	71% Epichlorohydrin	Propane, propylene
57. Allyl chloride	100% Propylene chlorination	Propane, propylene
72. Acrolein	100% Propylene oxidation	Propane, propylene
79. *n*-Butyraldehyde	100% Oxo process	Propane, propylene
86. n-Butanol (utyl alcohol)	80% Oxo process	Propane, propylene
93. Isobutyraldehyde	100% Oxo process	Propane, propylene
96. Acetylene	8% Ethylene by-product	Propane, propylene
98. *t*-Butanol	79% Propylene oxide co-product	Propane, propylene
101. Dodecene	100% Nonene co-product	Propane, propylene
106. Isobutanol (isobutyl alcohol)	100% Oxo process	Propane, propylene
118. Propyl alochol	13% Propane oxidation	Propane, propylene
124. Formic acid	98% *n*-Butane oxidation	Propane, propylene

Table C-1. (Continued)

Product	Process	Carrier Gas
	2-Carbon-Atom Reactants (Continued)	
16. Propylene	30% Refinery by-product	Ethane, ethylene
16. Propylene	54% Naptha/gas-oil pyrolysis	Ethane, ethylene
16. Propylene	16% Natural-gas liquids pyrolysis	Ethane, ethylene
18. Ethylene glycol	100% Ethylene oxide	Ethylene oxide
20. Cumene	100% Benzene	Ethane, ethylene
28. Acrylic acid	23% Modified Reppe	Ethylene, acetylene
29. Acetic acid	33% Acetaldehyde	Acetaldehyde
31. Alkyl leads	95% Ethyl chloride	Ethyl chloride
33. Ethyl chloride	4% Ethanol/ethane	Ethane, ethylene
33. Ethyl chloride	96% Ethylene chlorination	Ethane, ethylene
34. Ethanolamines	100% Ethylene oxide	Ethylene oxide
35. Vinyl acetate (VA)	13% Acetylene vapor phase	Ethylene, acetylene
35. Vinyl acetate (VA)	15% Ethylene liquid phase	Ethane, ethylene
35. Vinyl acetate (VA)	72% Ethylene vapor phase	Ethane, ethylene
37. 1,3-Butadiene	80% Ethylene co-product	Ethane, ethylene
50. Pentaerythritol	100% Formaldehyde/acetaldehyde	Acetaldehyde
53. Diethylene, triethylene glycols	100% Co-product w/ethylene glycol	Ethylene oxide
61. Pyridine	100% Formaldehyde/acetaldehyde	Acetaldehyde
63. Ethanol (ethyl alcohol)	100% Ethylene	Ethane, ethylene
65. Acetaldehyde	100% Ethylene	Ethane, ethylene
68. Glycol ethers	97% Ethylene oxide	Ethylene oxide
74. Methyl styrene	85% Cumene process by-product	Ethane, ethylene
76. Ethyl acrylate	61% Acetylene (Reppe)	Ethylene, acetylene
86. n-Butanol (butyl alcohol)	20% Acetaldehyde	Acetaldehyde
87. Propionic acid	93% Oxo process	Ethane, ethylene
89. Ethylene dibromide	100% Ethylene bromination	Ethane, ethylene
96. Acetylene	8% Ethylene by-product	Ethane, ethylene
118. Propyl alcohol	87% Oxo process	Ethane, ethylene
118. Propyl alcohol	13% Propane oxidation	Ethane, ethylene
120. Ethyl (diethyl) ether	100% Ethanol	Ethane, ethylene
122. Crotonaldehyde	100% Aldo process	Acetaldehyde
124. Formic acid	98% n-Butane oxidation	Ethane, ethylene
136. Amino ethylethanolamine	100% Ethylene oxide	Ethylene oxide

Table C-1. (Continued)

Product	Process	Carrier Gas
4-Carbon-Atom Reactants		
4.[b] Maleic anhydride	15% Butane oxidation	Butane, butylene
7. Ethylene	2% Refinery by-product	Butane, butylene
7. Ethylene	52% Natural-gas liquids pyrolysis	Butane, butylene
7. Ethylene	46% Naphtha/gas-oil pyrolysis	Butane, butylene
15. Propylene oxide	40% Peroxidation	Butane
16. Propylene	54% Naphtha/gas-oil pyrolysis	Butane, butylene
16. Propylene	16% Natural-gas liquids pyrolysis	Butane, butylene
16. Propylene	30% Refinery by-product	Butane, butylene
29. Acetic acid	44% Butane oxidation	Butane, butylene
30. Chloroprene	100% Via butadiene	Butadiene
37. 1,3-Butadiene	80% Ethylene co-product	Butane, butylene
37. 1,3-Butadiene	7% n-Butene	Butene
37. 1,3-Butadiene	13% n-Butane	Butane, butylene
58. Adiponitrile/HMDA	65% Butadiene	Butadiene
96. Acetylene	8% Ethylene by-product	Butane, butylene
98. t-Butanol	21% Isobutylene	Isobutylene
105. Methyl ethyl ketone (MEK)	25% Butane oxidation	Butane, butylene
118. Propyl alcohol	13% Propane oxidation	Butane, butylene
119. Butyl amines	100% Butyraldehyde hydrogenation	Butylene
124. Formic acid	98% n-Butane oxidation	Butane, butylene
134. Butyric acid	67% n-Butane oxidation	Butane, butylene
5-Carbon-Atom Reactants		
7. Ethylene	46% Naphtha/gas-oil pyrolysis	Pentene
7. Ethylene	2% Refinery by-product	Pentene
7. Ethylene	52% Natural-gas liquids pyrolysis	Pentene
16. Propylene	16% Natural-gas liquids pyrolysis	Pentene
16. Propylene	30% Refinery by-product	Pentene
16. Propylene	54% Naphtha/gas-oil pyrolysis	Pentene
37. 1,3-Butadiene	80% Ethylene co-product	Pentene
96. Acetylene	8% Ethylene by-product	Pentene

Table C-1. (Continued)

Product	Process	Carrier Gas
	Nitrogen-Containing Reactants	
1.[b] Vinyl chloride	1% Acetylene	
2. Acrylonitrile	100% Propylene oxidation	
3. Ethylene dichloride	50% Oxychlorination	
4. Maleic anhydride	15% Butane oxidation	
4. Maleic anhydride	85% Benzene oxidation	
5. Ethylene oxide	66% Air oxidation/ethylene	
6. Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid	
6. Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid	
6. Dimethyl terephthalate (DMT)	35% Du Pont	
6. Dimethyl terephthalate (DMT)	25% Hercules	
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	
9. Hydrogen cyanide (HCN)	50% Andrussow process	
13. Formaldehyde	77% Silver catalyst/methanol	
13. Formaldehyde	23% Metal oxide/methanol	
15. Propylene oxide	40% Peroxidation	
19. Cyclohexanol/cyclohexanone	75% Cyclohexane	
22. Phenol	2% Toluene oxidation	
22. Pehnol	93% Cumene	
26. Terephthalic acid (TPA)	39% Amoco	
26. Terephthalic acid (TPA)	14% Mobil	
26. Terephthalic aicd (TPA)	47% Eastman	
28. Acrylic acid	77% Propylene oxidation	
29. Acetic acid	44% Butane oxidation	
29. Acetic acid	33% Acetaldehyde	
32. Acetone	31% Isopropnol	
32. Acetone	69% Cumene	
34. Ethanolamines	100% Ethylene oxide	
37. 1,3-Butadiene	7% *n*-Butene	
41. Phthalic anhydride	70% *o*-Xylene	
41. Phthalic anhydride	30% Naphthalene	
58. Adiponitrile/HMDA	65% Butadiene	

Table C-1. (Continued)

Products	Process	Carrier Gas
	Nitrogen-Containing Reactants (Continued)	
65.[b] Acetaldehyde	100% Ethylene	
72. Acrolein	100% Propylene oxidation	
81. Acetophenone	40% Ethylbenzene oxidation	
81. Acetophenone	60% Cumene peroxidation	
82. Isophthalic acid	100% m-Xylene oxidation	
83. Benzoic acid	100% Toluene air oxidation	
94. Cresylic acids (SYN)	4% Cumene oxidation	
94. Cresylic acids (SYN)	80% Natural coal tar	
96. Acetylene	62% Hydrocarbon oxidation	
100. Dimethyl hydrazine	100% Nitrosodimethyl amine	
105. Methyl ethyl ketone (MEK)	25% Butane oxidation	
107. Hydroquinone	100% Acetone co-product	
118. Propyl alcohol	13% Propane oxidation	
124. Formic acid	98% n-Butane oxidation	
127. Isodecanol	25% n-Paraffin oxidation	
134. Butyric acid	33% Butyraldehyde oxidation	
134. Butyric acid	67% n-Butane oxidation	
	Argon-Containing Reactants	
5. Ethylene oxide	34% O_2 oxidation/ethylene	
35. Vinyl acetate (VA)	15% Ethylene liquid phase	
35. Vinyl acetate (VA)	72% Ethylene vapor phase	
	Hydrogen-Containing Reactants	
19. Cyclohexanol/cyclohexanone	25% Phenol	
21. Methanol (methyl alcohol)	100% Methane	
23. Aniline	100% Nitrobenzene hydrogenation	
37. 1,3-Butadiene	13% n-Butane	
44. Glycerol (synthetic only)	14% Acrolein	
46. Cyclohexane	84% Benzene hydrogenation	
58. Adiponitrile/HMDA	11% Acrylonitrile	
58. Adiponitrile/HMDA	65% Butadiene	
58. Adiponitrile/HMDA	24% Adipic acid	
60. Methyl isobutyl ketone (MIBK)	100% Acetone	
62. Benzene	20% Toluene hydrodealkylation	
79. n-Butyraldehyde	100% Oxo process	

Table C-1. (Continued)

Products	Process	Carrier Gas
Hydrogen-Containing Reactants (Continued)		
81.[b] Acetophenone	40% Ethylbenzene oxidation	
85. 2-Ethyl 1-hexanol	100% Condensation	
86. n-Butanol (butyl alcohol)	80% Oxo process	
86. n-Butanol (butyl alcohol)	20% Acetaldehyde	
87. Propionic acid	93% Oxo process	
93. Isobutylraldehyde	100% Oxo process	
106. Isobutanol (isobutyl alcohol)	100% Oxo process	
112. Biphenyl	100% Toluene hydrodealkylation	
118. Propyl alcohol	87% Oxo process	
119. Butyl amines	100% Butraldehyde hydrogenation	
123. Isooctyl alcohol	100% Oxo process/hydrogenation	
127. Isodecanol	75% Oxo process	
137. Cyclohexylamine	50% Cyclohexanone	
137. Cyclohexylamine	50% Aniline	
Carbon Monoxide—Containing Reactants		
21. Methanol (methyl alcohol)	100% Methane	
28. Acrylic acid	23% Modified Reppe	
29. Acetic acid	19% Methanol	
39. Toluene diisocyanate (TDI)	100% Diaminotoluene	
76. Ethyl acrylate	61% Acetylene (Reppe)	
79. n-Butyraldehyde	100% Oxo process	
85. 2-Ethyl 1-hexanol	100% Condensation	
86. n-Butanol (butyl alcohol)	80% Oxo process	
86. n-Butanol (butyl alcohol)	20% Acetaldehyde	
87. Propionic acid	93% Oxo process	
93. Isobutyraldehyde	100% Oxo process	
97. Phosgene	100% Carbon monoxide/chlorine	
106. Isobutanol (isobutyl alcohol)	100% Oxo process	
118. Propyl alcohol	87% Oxo process	
123. Isooctyl alcohol	100% Oxo process/hydrogenation	
127. Isodecanol	75% Oxo process	

Table C-1. (Continued)

Products	Process	Carrier Gas
	Oxygen-Containing Reactants	
2.[b] Acrylonitrile	100% Propylene oxidation	
4. Maleic anhydride	15% Butane oxidation	
4. Maleic anhydride	85% Benzene oxidation	
5. Ethylene oxide	34% O_2 Oxidation/ethylene	
5. Ethylene oxide	66% Air oxidation/ethylene	
6. Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid	
6. Dimethyl terephthalate (DMT)	35% Du Pont	
6. Dimethyl terephthalate (DMT)	25% Hercules	
6. Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid	
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	
9. Hydrogen cyanide (HCN)	50% Andrussow process	
13. Formaldehyde	77% Silver catalyst/methanol	
13. Formaldehyde	23% Metal oxide/methanol	
15. Propylene oxide	40% Peroxidation	
19. Cyclohexanol/cyclohexanone	75% Cyclohexane	
22. Phenol	93% Cumene	
22. Phenol	2% Toluene oxidation	
26. Terephthalic acid (TPA)	14% Mobil	
26. Terephthalic acid (TPA)	39% Amoco	
26. Terphthalic acid (TPA)	47% Eastman	
28. Acrylic acid	77% Propylene oxidation	
29. Acetic acid	44% Butane oxidation	
29. Acetic acid	33% Acetaldehyde	
32. Acetone	31% Isopropanol	
32. Acetone	69% Cumene	
35. Vinyl acetate (VA)	72% Ethylene vapor phase	
37. 1,3-Butadiene	7% n-Butene	
41. Phthalic anhydride	30% Naphthalene	
41. Phthalic anhydride	70% o-Xylene	
58. Adiponitrile/HMDA	65% Butadiene	
65. Acetaldehyde	100% Ethylene	
72. Acrolein	100% Propylene oxidation	

Table C-1. (Continued)

Products	Processes	Carrier Gas
	Oxygen-Containing Reactants (Continued)	
81.[b] Acetophenone	40% Ethyl benzene oxidation	
81. Acetophenone	60% Cumene peroxidation	
82. Isophthalic acid	100% m-Xylene oxidation	
83. Benzoic adid	100% Toluene air oxidation	
94. Cresylic acids (SYN)	4% Cymene oxidation	
94. Cresylic acids (SYN)	80% Natural coal tar	
96. Acetylene	62% Hydrocarbon oxidation	
100. Dimethyl hydrazine	100% Nitrosodimethyl amine	
105. Methyl ethyl ketone (MEK)	25% Butane oxidation	
107. Hydroquinone	100% Acetone co-product	
118. Propyl alcohol	13% Propane oxidation	
124. Formic acid	98% n-Butane oxidation	
127. Isodecanol	25% n-Paraffin oxidation	
134. Butyric acid	33% Butyraldehyde oxidation	
134. Butyric acid	67% n-Butane oxidation	
	Chlorine-Containing Reactants	
1. Vinyl chloride	1% Acetylene	
3. Ethylene dichloride	50% Oxychlorination	
3. Ethylene dichloride	50% Direct chlorination	
11. 1,1,1-Trichloroethane	74% Vinyl chloride	
11. 1,1,1-Trichloroethane	10% Ethane chlorination	
12. Carbon tetrachloride	38% Carbon disulfide	
12. Carbon tetrachloride	42% Chloroparaffin chlorinolysis	
12. Carbon tetrachloride	20% Methane	
15. Propylene oxide	60% Chlorohydrin	
25. Perchloroethylene	66% Ethylene dichloride	
25. Perchloroethylene	34% Ethane chlorinolysis	
27. Chlorobenzene	100% Benzene chlorination	
30. Chloroprene	100% Via butadiene	
33. Ethyl chloride	4% Ethanol/ethane	
33. Ethyl chloride	96% Ethylene chlorination	
35. Vinyl acetate (VA)	15% Ethylene liquid phase	

Table C-1. (Continued)

Products	Processes	Carrier Gas
Chlorine-Containing Reactants (Continued)		
36.[b] Methylene chloride	65% Methanol/methyl chloride	
36. Methylene chloride	35% Methane chlorination	
40. Chloroform	61% Methane chlorination	
40. Chloroform	39% Methanol chlorination	
44. Glycerol (synthetic only)	15% Allyl alcohol	
44. Glycerol (synthetic only)	71% Epichlorohydrin	
56. Epichlorohydrin	100% Allyl chloride/HCl	
57. Allyl chloride	100% Propylene chlorination	
59. Trichloroethylene	91% Ethylene dichloride	
77. Methyl chloride	2% Methane chlorination	
91. Benzeyl chloride	100% Toluene chlorination	
92. Dichlorophenol	45% Phenol chlorination	
97. Phosgene	100% Carbon monoxide/chlorine	
113. Acetyl chloride	100% Sodium acetate	
115. Chloroacetic acid	100% Acetic acid chlorination	
132. Hexachlorobenzene	100% Hexachlorocyclohexane	
Bromine-Containing Reactants		
82. Isophthalic acid	100% m-Xylene oxidation	
89. Ethylene dibromide	100% Ethylene bromination	
117. Methyl bromide	100% Methanol/HBR and bromine	
Carbon Dixide—Containing Reactants		
21. Methanol (methyl alcohol)	100% Methane	
28. Acrylic acid	23% Modified Reppe	
29. Acetic acid	19% Methanol	
64. Urea	100% Ammonia/carbon dioxide	
76. Ethyl acrylate	61% Acetylene (Reppe)	
94. Cresylic acids (SYN)	80% Natural coal tar	
99. Salicylic acid	100% Sodium phenate	

Table C-1. (Continued)

Products	Process	Carrier Gas
	Sulfur Trioxide-Containing Reactants	
22.[b] Phenol	2% Benzene sulfonation	
126. Linear alkyl benzene sulfonate	100% Lab sulfonation	
138. Toluene sulfonic acids	100% Toluene sulfonation	
	Hydrogen Chloride-Containing Reactants	
11. 1,1,1-Trichloroethane	10% Ethane chlorination	
11. 1,1,1-Trichloroethane	16% Vinylidene chloride	
11. 1,1,1-Trichloroethane	74% Vinyl chloride	
22. Phenol	3% Chlorobenzene	
59. Trichloroethylene	9% Acetylene	
73. Diphenylamine	100% Aniline amination	
75. Ethylene diamine/triethylene tetramine	100% EDC ammonolysis	
77. Methyl chloride	98% Methanol hydrochlorination	
99. Salicylic acid	100% Sodium phenate	
116. Benzophenone	100% Benzene/carbon tetrachloride	
	Hydrogen Bromide-Containing Reactant	
117. Methyl bromide	100% Methanol/HBR and bromine	
	Hydrogen Fluoride-Containing Reactants	
24. Fluorocarbons	100% CCl_4/C_2Cl_6 fluorination	
71. Linear alkyl benzene	100% Benzene alkylation	
	Ammonia-Containing Reactants	
2. Acrylonitrile	100% Propylene oxidation	
9. Hydrogen cyanide (HCN)	50% Andrussow process	
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	
34. Ethanolamines	100% Ethylene oxide	
49. Caprolactam	100% Cyclohexanone	
52. Acrylamide	100% Acrylonitrile	
58. Adiponitrile/HMDA	24% Adipic acid	
61. Pyridine	100% Formaldehyde/acetaldehyde	
64. Urea	100% Ammonia/carbon dioxide	
75. Ethylene diamine/triethylene tetramine	100% DC ammonolysis	
80. Nitroaniline	100% Nitro chlorobenzene	
100. Dimethyl hydrazine	100% Nitrosodimethyl amine	

Table C-1. (Continued)

	Products	Process	Carrier Gas
		Ammonia-Containing Reactants (Continued)	
108.[b]	Mono-, di-, trimethyl amines	100% Methanol ammonolysis	
114.	Mono-, di-, trimethyl amine	100% Ethanol ammonolysis	
119.	Butyl amines	100% Butryaldehyde hydrogenation	
121.	Propyl amines (M-D-T)	50% n-Propyl alcohol	
121.	Propyl amines (M-D-T)	50% n-Propyl chloride	
137.	Cyclohexylamine	50% Cyclohexanone	
		Miscellaneous Gaseous	
17.	Nitrobenzene	100% Benzene nitration	Nitrogen oxides
39.	Toluene diisocyanate (TDI)	100% Diaminotoluene	Nitrogen oxides, phosgene
43.	Acetic anhydride	100% Acetic acid	Ketene
49.	Caprolactam	100% Cyclohexanone	Hydroxylamine
78.	Methylene diphenylene diisocynate	100% DPMDA/phosgene	Phosgene
109.	Adipic acid	100% Cyclohexane	Nitrogen oxides
110.	Chloronitrobenzene	100% Chlorobenzene nitra-	Nitrogen oxides

Table C-2. Various Product Carrier Gases[a]

Product	Process	Carrier Gas
	1-Carbon-Atom Products	
2.[b] Acrylonitrile	100% Propylene oxidation	Hydrogen cyanide
7. Ethylene	2% Refinery by-product	Methane
7. Ethylene	52% Natural gas liquids pyrolysis	Methane
7. Ethylene	46% Naphtha gas-oil pyrolysis	Methane
9. Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	Hydrogen cyanide
9. Hydrogen cyanide (HCN)	50% Andrussow process	Hydrogen cyanide
12. Carbon tetrachloride	20% Methane	Methyl chloride
13. Formaldehyde	77% Silver catalyst/methanol	Formaldehyde
13. Formaldehyde	23% Metal oxide/methanol	Formaldehyde
14. Methyl methacrylate (MMA)	100% Acetone cyanohydrin	Hydrogen cyanide
16. Propylene	54% Naphtha/gas-oil pyrolysis	Methane
16. Propylene	30% Refinery by-product	Methane
16. Propylene	16% Natural-gas liquids pyrolysis	Methane
24. Fluorocarbons	100% CCl_4/C_2Cl_6 fluorination	Fluorinated methanes
62. Benzene	20% Toluene hydrodealkylation	Methane
77. Methyl chloride	2% Methane chlorination	Methyl chloride
77. Methyl chloride	98% Methanol hydrochlorination	Methyl chloride
96. Acetylene	8% Ethylene by-product	Methane
97. Phosgene	100% Carbon monoxide/chlorine	Methyl chloride
108. Mono-, di-, trimethyl amines	100% Methanol ammonolysis	Methyl amine
112. Biphenyl	100% Toluene hydrodealkylation	Methane
117. Methyl bromide	100% Methanol/HBR and bromine	Methyl bromide
	2-Carbon-Atom Products	
1. Vinyl chloride	1% Acetylene	Vinyl chloride
1. Vinyl chloride	99% Ethylene dichloride	Vinyl chloride
3. Ethylene dichloride	50% Oxychlorination	Ethyl chloride
3. Ethylene dichloride	50% Direct chlorination	Ethyl chloride
5. Ethylene oxide	66% Air oxidation/ethylene	Ethylene oxide
5. Ethylene oxide	34% O_2 oxidation/ethylene	Ethylene oxide
7. Ethylene	46% Naphtha gas-oil pyrolysis	Ethane, ethylene

---

[a] See Table III-4.

[b] Refers to rank-order number in Table III-4.

Table C-2. (Continued)

Product	Process	Carrier Gas
	2-Carbon-Atom Products (Continued)	
7. Ethylene	2% Refinery by-product	Ethane, ethylene
7. Ethylene	52% Natural gas liquids pyrolysis	Ethane, ethylene
16. Propylene	30% Refinery by-product	Ethane, ethylene
16. Propylene	54% Naphtha/gas-oil pyrolysis	Ethane, ethylene
16. Propylene	16% Natural-gas liquids pyrolysis	Ethane, ethylene
24. Fluorocarbons	100% CCl_4/C_2Cl_6 fluorination	Fluorinated ethanes
33. Ethyl chloride	4% Ethanol/ethane	Ethyl chloride
33. Ethyl chloride	96% Ethylene chlorination	Ethyl chloride
35. Vinyl acetate (VA)	72% Ethylene vapor phase	Acetaldehyde
35. Vinyl acetate (VA)	15% Ethylene liquid phase	Acetaldehyde
65. Acetaldehyde	100% Ethylene	Acetaldehyde
96. Acetylene	30% Calcium carbide	Acetylene
96. Acetylene	62% Hydrocarbon oxidation	Acetylene
96. Acetylene	8% Ethylene by-product	Acetylene
124. Formic acid	98% n-Butane oxidation	Methyl formate
	3-Carbon-Atom Products	
16. Propylene	54% Naphtha/gas-oil pyrolysis	Propylene
16. Propylene	30% Refinery by-product	Propylene
16. Propylene	16% Natural-gas liquids pyrolysis	Propylene
	4-Carbon-Atom Products	
37. 1,3-Butadiene	80% Ethylene co-product	Butyne, butadiene
37. 1,3-Butadiene	7% n-Butene	Butyne, butadiene
37. 1,3-Butadiene	13% n-Butane	Butyne, butadiene
	Hydrogen-Containing Products	
7. Ethylene	46% Naptha gas oil pyrolysis	
7. Ethylene	2% Refinery by-product	
7. Ethylene	52% Natural gas liquids pyrolysis	
10. Styrene	Ethylbenzene	
16. Propylene	16% Natural gas liquids pyrolysis	

Table C-2. (Continued)

	Product	Process	Carrier Gas
		Hydrogen-Containing Products (Continued)	
16.	Propylene	30% Refinery by-product	
16.	Propylene	54% Naphtha/gas-oil pyrolysis	
21.	Methanol (methyl alcohol)	100% Methane	
29.	Acetic acid	4% Others	
32.	Acetone	31% Isopropanol	
37.	1,3-Butadiene	80% Ethylene co-product	
37.	1,3-Butadiene	7% n-Butene	
61.	Pyridine	100% Formaldehyde/acetaldehyde	
66.	Isoprene	33% Isoamylene extraction	
66.	Isoprene	67% C_4 hydrocarbons	
71.	Linear alkyl benzene	100% Benzene alkylation	
74.	Methyl styrene	15% Cumene dehydrogenation	
96.	Acetylene	62% Hydrocarbon oxidation	
96.	Acetylene	8% Ethylene by-product	
105.	Methyl ethyl ketone (MEK)	75% Sec-butanol	
107.	Hydroquinone	100% Acetone co-product	
131.	Cyclooctadiene	100% Butadiene dimerization	
132.	Hexachlorobenzene	100% Hexachlorocyclohexane	
		Carbon Monoxide-Containing Products	
2.	Acrylonitrile	100% Propylene oxidation	
4.	Maleic anhydride	15% Butane oxidation	
4.	Maleic anhydride	85% Benzene oxidation	
5.	Ethylene oxide	66% Air oxidation/ethylene	
6.	Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid	
6.	Dimethyl terephthalate (DMT)	25% Hercules	
6.	Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid	
6.	Dimethyl terephthalate (DMT)	35% Du Pont	
9.	Hydrogen cyanide (HCN)	50% Acrylonitrile co-product	
21.	Methanol (methyl alcohol)	100% Methane	
26.	Terephthalic acid (TPA)	39% Amoco	
26.	Terephthalic acid (TPA)	14% Mobil	
26.	Terephthalic acid (TPA)	47% Eastman	

Table C-2. (Continued)

	Product	Process
	Carbon Monoxide-Containing Products (Continued)	
41.	Phthalic anhydride	30% Naphthalene
41.	Phthalic anhydride	70% o-Xylene
72.	Acrolein	100% Propylene oxidation
96.	Acetylene	62% Hydrocarbon oxidation
	Carbon Dioxide-Containing Products	
2.	Acrylonitrile	100% Propylene oxidation
4.	Maleic anhydride	15% Butane oxidation
4.	Maleic anhydride	85% Benzene oxidation
5.	Ethylene oxide	34% O_2 Oxidation/ethylene
5.	Ethylene oxide	66% Air oxidation/ethylene
6.	Dimethyl terephthalate (DMT)	23% Amoco via terephthalic acid
6.	Dimethyl terephthalate (DMT)	35% Du Pont
6.	Dimethyl terephthalate (DMT)	25% Hercules
6.	Dimethyl terephthalate (DMT)	17% Eastman via terephthalic acid
9.	Hydrogen cyanide (HCN)	50% Acrylonitrile co-product
21.	Methanol (methyl alcohol)	100% Methane
22.	Phenol	2% Toluene oxidation
26.	Terephthalic acid (TPA)	14% Mobil
26.	Terephthalic acid (TPA)	47% Eastman
26.	Terephthalic acid (TPA)	39% Amoco
28.	Acrylic acid	77% Propylene oxidation
30.	Chloroprene	100% Via butadiene
35.	Vinyl acetate (VA)	72% Ethylene vapor phase
35.	Vinyl acetate (VA)	15% Ethylene liquid phase
40.	Chloroform	39% Methanol chlorination
41.	Phthalic anhydride	30% Naphthalene
41.	Phthalic anhydride	70% o-Xylene
44.	Glycerol (synthetic only)	71% Epichlorohydrin
72.	Acrolein	100% Propylene oxidation

Table C-2. (Continued)

Product	Process
	Sulfur Trioxide-Containing Products
22. Phenol	2% Benzene sulfonation
49. Caprolactam	100% Cyclohexanone
	Hydrogen Chloride-Containing Products
1. Vinyl chloride	99% Ethylene dichloride
8. Ethylbenzene	98% Benzene alkylation
11. 1,1,1-Trichloroethane	74% Vinyl chloride
11. 1,1,-Trichloroethane	10% Ethane chlorination
12. Carbon tetrachloride	42% Chloroparaffin chlorinolysis
12. Carbon tetrachloride	20% Methane
15. Propylene oxide	60% Chlorohydrin
24. Fluorocarbons	100% CCl_4/C_2Cl_6 fluorination
25. Perchloroethylene	66% Ethylene dichloride
25. Perchloroethylene	34% Ethane chlorinolysis
27. Chlorobenzene	100% Benzene chlorination
30. Chloroprene	100% Via butadiene
31. Alkyl leads	95% Ethyl chloride
33. Ethyl chloride	4% Ethanol/ethane
33. Ethyl chloride	96% Ethylene chlorination
36. Methylene chloride	35% Methane chlorination
36. Methylene chloride	65% Methanol/methyl chloride
38. Vinylidene chloride	50% 1,1,1-Trichloroethylene
38. Vinylidene chloride	50% 1,1,2-Trichloroethylene
39. Toluene diisocyanate (TDI)	100% Diaminotoluene
40. Chloroform	61% Methane chlorination
44. Glycerol (synthetic only)	71% Epichlorohydrin
57. Allyl chloride	100% Propylene chlorination
59. Trichloroethylene	91% Ethylene dichloride
59. Trichloroethylene	9% Acetylene
65. Acetaldehyde	100% Ethylene
91. Benzyl chloride	100% Toluene chlorination
92. Dichlorophenol	45% Phenol chlorination

Table C-2. (Continued)

	Product	Process	Carrier Gas
		Hydrogen Chloride-Containing Products (Continued)	
92.	Dichlorophenol	55% Trichlorobenzene	
113.	Acetyl chloride	100% Sodium acetate	
115.	Chloroacetic acid	100% Acetic acid chlorination	
116.	Benzophenone	100% Benzene/carbon tetrachloride	
132.	Hexachlorobenzene	100% Hexachlorocyclohexane	
136.	Amino ethylethanolamine	100% Ethylene oxide	
140.	Benzoyl chloride	100% Benzoic acid	
		Miscellaneous Gaseous Products	
19.	Cyclohexanol/cyclohexanone	75% Cyclohexane	Nitrogen oxides
43.	Acetic anhydride	100% Acetic acid	Ketene
45.	Nitrophenol	100% Phenol nitration	Nitrogen oxides
51.	Nonyl phenol	100% Phenol alkylation	Boron trifluoride
69.	Dinitrotoluene	100% Toluene dinitration	Nitrogen oxides
97.	Phosgene	100% Carbon monoxide/chlorine	Phosgene
135.	Dinitrophenol	100% Dinitration of phenol	Nitrogen oxides

APPENDIX D

SAMPLE CALCULATIONS

SAMPLE CALCULATIONS

The sample calculation will be for 1,1,1-trichloroethane from ethane.

1. Chlorine Carrier Gases

a. Merchant Chlorine

$C = MCR \times (F_C - 1) \times (1 - S_C) + MCR \times (1 - P_C) \times F_C + 2 \times (1 - S_{In})$

$C_{min} = 3 \times 0 \times 0.001 + 3 \times 0.006 \times 1.0 \times 0.5 = 0.009$

$C_{max} = 3 \times 0.3 \times 0.05 + 3 \times 0.025 \times 1.3 \times 0.9 = 0.133$

b. Captive Chlorine

$C_{min} = 3 \times 0 \times 0.001 + 3 \times 0.01 \times 1.0 \times 0.5 = 0.015$

$C_{max} = 3 \times 0.3 \times 0.05 + 3 \times 0.10 \times 1.3 \times 0.9 = 0.396$

2. Hydrogen Chloride Carrier Gases

$H = MHCR \times (1 - S_H)$

$H_{min} = 1 \times 0.01 = 0.01$

$H_{max} = 3 \times 0.10 = 0.30$

3. Gaseous Organic Reactant Carrier Gases

$R = MGRR \times F_{GR} \times (1 - Y_{GR}) \times (1 - S_{GR})$

$R_{min} = 1 \times 0.9 \times 0.01 \times 0.1 = 0.0009$

$R_{max} = 1 \times 1.0 \times 0.20 \times 0.9 = 0.180$

4. Gaseous Organic Product Carrier Gases

$P = MGPR \times (1 - S_{GP})$

$P_{min} = 0.33 \times 0.1 = 0.033$

$P_{max} = 0.33 \times 0.9 = 0.297$

5. Total Carrier Gases

a. Merchant Chlorine

$$G = C_{min} + H_{min} + R_{min} + P_{min}$$

$$G_{min} = 0.009 + 0.01 + 0.0009 + 0.033 = 0.0529$$

$$G_{max} = 0.133 + 0.30 + 0.180 + 0.297 = 0.910$$

b. Captive Chlorine

$$G_{min} = 0.015 + 0.01 + 0.0009 + 0.033 = 0.0589$$

$$G_{max} = 0.396 + 0.30 + 0.180 + 0.297 = 1.173$$

6. Conversion to scfm/$\bar{M}$ lb/yr of Product (for the Merchant-Chlorine Case)

Basis: 1 $\bar{M}$ lb/yr of product

$$G_{min}\left(\frac{\text{scfm}}{\bar{M}\ \text{lb/yr product}}\right) = G_{min}\left(\frac{\text{moles of gas}}{\text{moles of product}}\right) \times \frac{359\ \text{scf}}{1\ \text{lb-mole of gas}} \times$$

$$\frac{1\ \text{mole of product}}{133.5\ \text{lb}} \times \frac{1 \times 10^6\ \text{lb}}{\text{yr}} \times \frac{1\ \text{yr}}{525{,}600\ \text{min}}$$

$$0.271\ \frac{\text{scfm}}{\bar{M}\ \text{lb/yr}} = 0.0529 \times 683/133.5$$

		$G\left(\frac{\text{scfm}}{\bar{M}\ \text{lb/yr of product}}\right)$	$G\left(\frac{\text{moles of gas}}{\text{mole of product}}\right)$
Merchant Cl_2	Min	0.272	0.0529
	Max	4.66	0.910
Captive Cl_2	Min	0.301	0.0589
	Max	6.02	1.173

7. Calculation of Carrier-Gas VOC

Reactant or Product

$$R\left(\frac{\text{moles of gas}}{\text{mole of product}}\right) \times 683/MW_{\text{product}} = R\left(\frac{\text{scfm}}{\bar{M}\ \text{lb/yr of product}}\right)$$

$$R\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb product}}\right) = R\left(\frac{\text{scfm}}{\bar{M}\text{ lb/yr of product}}\right) \times 1463 \times MW_{VOC}$$

$$\text{Total carrier-gas VOC} = R\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb of product}}\right) + P\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb of product}}\right)$$

(Take the minimum case)

$$\text{Reactant} - 0.0009 \times 683/133.5 = 0.0046\left(\frac{\text{scfm}}{\bar{M}\text{ lb/yr of product}}\right)$$

$$0.0046 \times 1463 \times 28 \text{ (assume propane)} = 188\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb of product}}\right)$$

$$\text{Product} = 0.033 \times 683/133.5 = 0.170\left(\frac{\text{scfm}}{\bar{M}\text{ lb/yr of product}}\right)$$

$$0.170 \times 1463 \times 64.5 \text{ (assume ethyl chloride)} = 16{,}030\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb of product}}\right)$$

$$\text{Total} = 188 + 16{,}030 = 16{,}218\left(\frac{\text{lb of VOC}}{\bar{M}\text{ lb of product}}\right)$$

8. Calculation of VOC from Organic Liquids and Solids

Organic liquid [scfm/($\bar{M}$ lb/yr)] = Carrier-gas flow [scfm/($\bar{M}$ lb/yr)] X

$$\frac{Y_{VOC}}{1 - Y_{VOC}}$$

(if $Y_{VOC} = 0.137$ for 1,1,1-trichloroethane at 21°C)

0.043 (low) = 0.272 (low) X 0.159

0.953 (high) = 6.02 (high) X 0.159

This is converted to lb of VOC/$\bar{M}$ lb of product by multiplying by the VOC molecular weight and 1463

0.043 X 133.5 X 1463 = 8398 (lb of VOC/$\bar{M}$ lb of product)

0.953 X 133.5 X 1463 = 186,130 (lb of VOC/$\bar{M}$ lb of product)

Values in Table IV-3 have been rounded.

REPORT 3

AIR OXIDATION EMISSION PROJECTION

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I. THE GENERIC STANDARD APPROACH

For a discussion of the basis for the generic standard concept see the report in this volume entitled "The Generic Standard Approach." The reader is advised to read this report since the concept and essential terminology is explained therein.

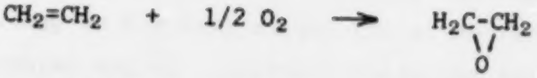
II. AIR-OXIDATION PROCESSES IN THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY

A. DESCRIPTION

Oxidation chemistry is widely practiced in SOCMI. Oxidation reactions take many forms, including the direct addition of oxygen into another compound, increasing the proportion of electronegative elements in a compound, removing one or more electrons from a compound, or dehydrogenating through the action of oxygen on a compound. Sometimes additional reactants are introduced with the oxygen in order to create other compounds, in which a case oxidation is part of the reaction mechanism but other types of chemical reactions also occur.

A few examples of oxidation reactions are shown below:

Ethylene Oxide



$CH_2{=}CH_2 + 1/2\ O_2 \rightarrow H_2C{-}CH_2$ (bridged by O)

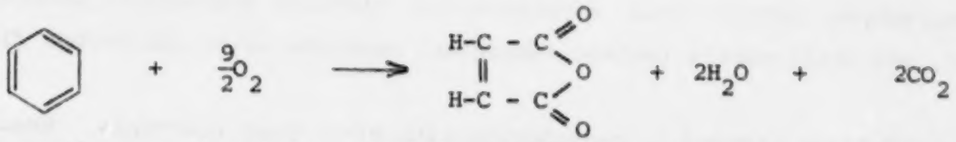
(ethylene) (oxygen) (ethylene oxide)

Formaldehyde

$CH_3OH + 1/2\ O_2 \rightarrow HCHO + H_2O$

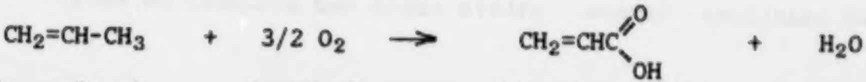
(methanol) (oxygen) (formaldehyde) (water)

Maleic Anhydride



(benzene) (oxygen) (maleic anhydride) (water) (carbon dioxide)

Acrylic Acid (reaction simplified—actually involves acrolein as an intermediate)



$CH_2{=}CH{-}CH_3 + 3/2\ O_2 \rightarrow CH_2{=}CHC(=O)OH + H_2O$

(propylene) (oxygen) (acrylic acid) (water)

Acrylonitrile

$$\underset{\text{(propylene)}}{CH_2{=}CH{-}CH_3} + \underset{\text{(ammonia)}}{NH_3} + \underset{\text{(oxygen)}}{3/2\ O_2} \longrightarrow \underset{\text{(acrylonitrile)}}{CH_2{=}CH{-}CN} + \underset{\text{(water)}}{3H_2O}$$

Ethylene Dichloride

$$\underset{\text{(ethylene)}}{2CH_2{=}CH_2} + \underset{\text{(hydrogen chloride)}}{4HCl} + \underset{\text{(oxygen)}}{O_2} \longrightarrow \underset{\text{(ethylene dichloride)}}{2ClCH_2CH_2Cl} + \underset{\text{(water)}}{2H_2O}$$

A wide variety of reactants can be used in oxidation processes. The starting chemicals can be aliphatic (ethylene or propylene) or aromatic (benzene) or they can be substituted hydrocarbons (methanol). Most oxidation processes use air as the oxygen source, some use oxygen-carrying catalysts (such as nitric acid in cyclohexanol-cyclohexanone), and others use purified oxygen. The mechanism of emission generation from oxygen oxidations relates to carrier gases introduced in trace quantities in the oxygen feed and to generation of carrier gases (CO and CO_2) in the oxidation reaction. Oxygen oxidation processes can be handled through the emission projection report on chemical reactions. This report deals only with oxidation processes (including ammoxidation and oxychlorination) that use air as the source of oxygen. Air-oxidation processes correspond most closely to the emission mechanism by which carrier gases are introduced with the reactants.

Some oxidations generate no reaction off-gases (ethylene oxide) whereas others (formaldehyde, acrylic acid, acrylonitrile, ethylene dichloride) generate water, and still others (maleic anhydride) generate water and carbon dioxide.

Some oxidations proceed in conjunction with other feed reactants. When ammonia is added to propylene and oxygen, ammoxidation occurs and acrylonitrile is produced. When hydrogen chloride is added to ethylene and oxygen, oxychlorination forms ethylene dichloride. These are the two most important oxidation related reactions; however, others could and probably do exist.

B. DISTRIBUTION OF AIR-OXIDATION PROCESSES IN SOCMI

The Survey and Ranking Program established that 140 compounds account for an estimated 86% of the SOCMI VOC emissions and identified the unit processes and unit operations associated with each ranked compound. Even though the emissions projected include storage and fugitive emissions, the relative values clearly identify the highest emitters from a unit process aspect as oxidation and ammoxidation. Oxychlorination also ranks high. The unit process ranking, Table II-1, shows that VOC emissions associated with oxidation account for a quarter of the total from the 140 compounds ranked and for approximately 24% of the 141 processes classed as high emitters.

Table II-2 lists some of the chemicals produced by oxidation processes in their order as ranked during the IT Enviroscience study. The number of sites producing this chemical and the average capacity of the individual sites are also listed. The prominence of the oxidation process is further displayed by the histogram of Fig. II-1, which shows that oxidation products (including ammoxidation and oxychlorination) account for 40% of the top 20 products in terms of emission severity and that they occur throughout the products ranked.[1]

Table II-1. Unit Process Ranking[a]

Unit Process	Number of Processes with High Emissions (>0.01% of Projected Total)	Total Number of Processes Ranked	Estimated Percent of Total Emissions (1982 Projection)
Oxidation	30	42	25.29
Ammoxidation	2	3	17.00
Pyrolysis	8	11	7.74
Chlorination	18	29	6.74
Esterification	11	17	5.59
Oxychlorination	2	3	4.18
Dehydrochlorination	5	8	3.77
Alkylation	3	7	3.20
Saponification	1	2	2.76
Hydrolysis	3	10	1.86
Hydrogenation	5	19	1.51
Hydration	7	9	1.44
Oxyacetylation	2	2	0.97
Dehydration	3	6	0.47
Hydroformulation	6	9	0.45
Phosgenation	2	2	0.43
Hydrobromination	3	5	0.41
Ammonolysis	5	11	0.39
Carbonylation	2	4	0.38
Nitration	4	4	0.37
Hydrochlorination	2	4	0.32
Condensation	3	5	0.31
Sulfonation	2	8	0.25
Dehydrogenation	5	6	0.17
Addition ester	1	1	0.14
Neutralization	2	6	0.08
Bromination	1	2	0.07
Peroxidation	2	3	0.06
Hydrocyanation	1	1	0.03
Reduction, cleaving, acidification, fusion, reforming, hydrodimerization, fluoronation, alcoholysis, and hydrodealkylation	0	0	0.00
Total	141	239	86.03[b]

---

[a] Based on total emissions, per HI survey and ranking program; includes estimate of fugitive, storage, secondary, and process emissions; when more than one process is used, the emisson estimate is proportioned.

[b] The 140 products ranked account for 86% of the estimated SOCMI emissions.

Table II-2. Chemicals Produced by Oxidation Processes

Chemicals	Hydroscience Ranking	Number of Production Sites	Average Site Capacity (M lb/yr)
Acrylonitrile[a]	2	6	358
Ethylene dichloride[b]	3	17	625
Maleic anhydride	4	10	51
Ethylene oxide	5	16	561
Dimethyl terephthlate[c]	6	6	693
Formaldehyde	13	54	76
Propylene oxide	15	6	386
Cyclohexanol/cyclohexanone	19	8	190
Phenol	22	13	275
Terephthalic acid[d]	26	3	517
Acrylic acid	28	3	251
Acetic acid	29	7	374
Acetone (phenol process)	32		164
Phthalic anhydride	41		
Acetaldehyde	65	3	400
Acrolein	72	2	60
Acetophenone	81		
Isophthalic acid	82		
Benzoic acid	83	5	51
Propionic acid	87	3	67
Cresylic acids	94		
t-Butyl alcohol	98		
Methyl ethyl ketone	105	2	90
Adipic acid	109		
Formic acid	124	4	19
Butyric acid	134		

[a] Ammoxidation process.

[b] Oxychlorination process.

[c] Dimethyl terephthalate is an ester of terephtalic acid which is produced by air oxidation.

[d] Terephthalic acid reported here does not include terephthalic acid used in the production of dimethyl terephthalate.

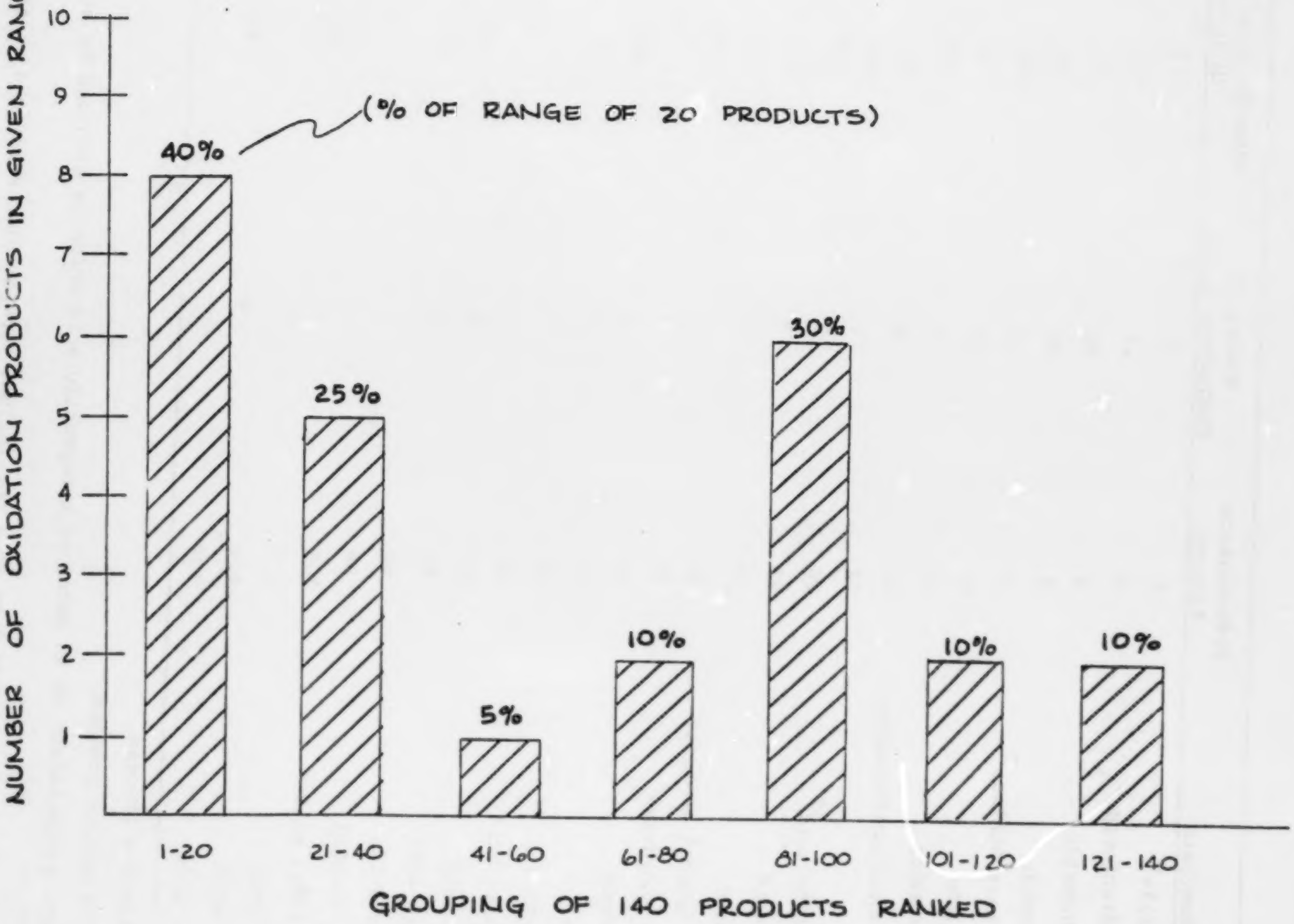


Fig. II-1. Occurrence Histogram of Oxidation Products Ranked

III. EMISSIONS

A. AIR-OXIDATION PROCESSES

With regard to the influence of air-oxidation processes on VOC emissions, the most important feature that they have in common is the requirement that air be contacted with organic reactants. The nitrogen in the air fed to the reactors must ultimately be released to the atmosphere, along with any other carrier gases. Air-oxidation processes can be liquid or vapor phase and can be carried out over a wide range of temperatures and pressures. Reactors may be the fixed-bed or fluidized-bed type. Single reactors or multiple reactors may be employed, with several possible gas stream recycle options. Many of these factors can affect VOC emissions.

In vapor-phase oxidations the gases leaving the reactor contain all of the vapor-phase product, as well as any unreacted reactants or other carrier gases. Chemical processing equipment must then be used to separate the product from the other gases. Most air-oxidation processes employ water or aqueous absorption to accomplish this separation. Some organic components may not be soluble in water, and sometimes absorbers using nonvolatile organics as the absorption fluid are used instead of, or in addition to, water product-recovery absorbers. Liquid-phase air-oxidation processes normally employ condensers, absorbers, or other devices to reduce the organic content of the gases leaving the reactors.

B. FLOW RATE

All air-oxidation processes have in common the ultimate atmospheric release of the carrier gases entering with the air, excess oxygen, gases formed during the reaction, and nonseparable organics at near-atmospheric pressure. The general oxidation process is shown in Fig. III-1. Process details beyond this general framework are not needed to estimate the range of flow rates from air-oxidation processes. Emission projections by the described technical approach apply to essentially all air-oxidation reactions without regard for process details or operating condition variables.

The total flow of gases emitted from any air oxidation process may be divided into three classifications: (1) One group is the gases that enter with the

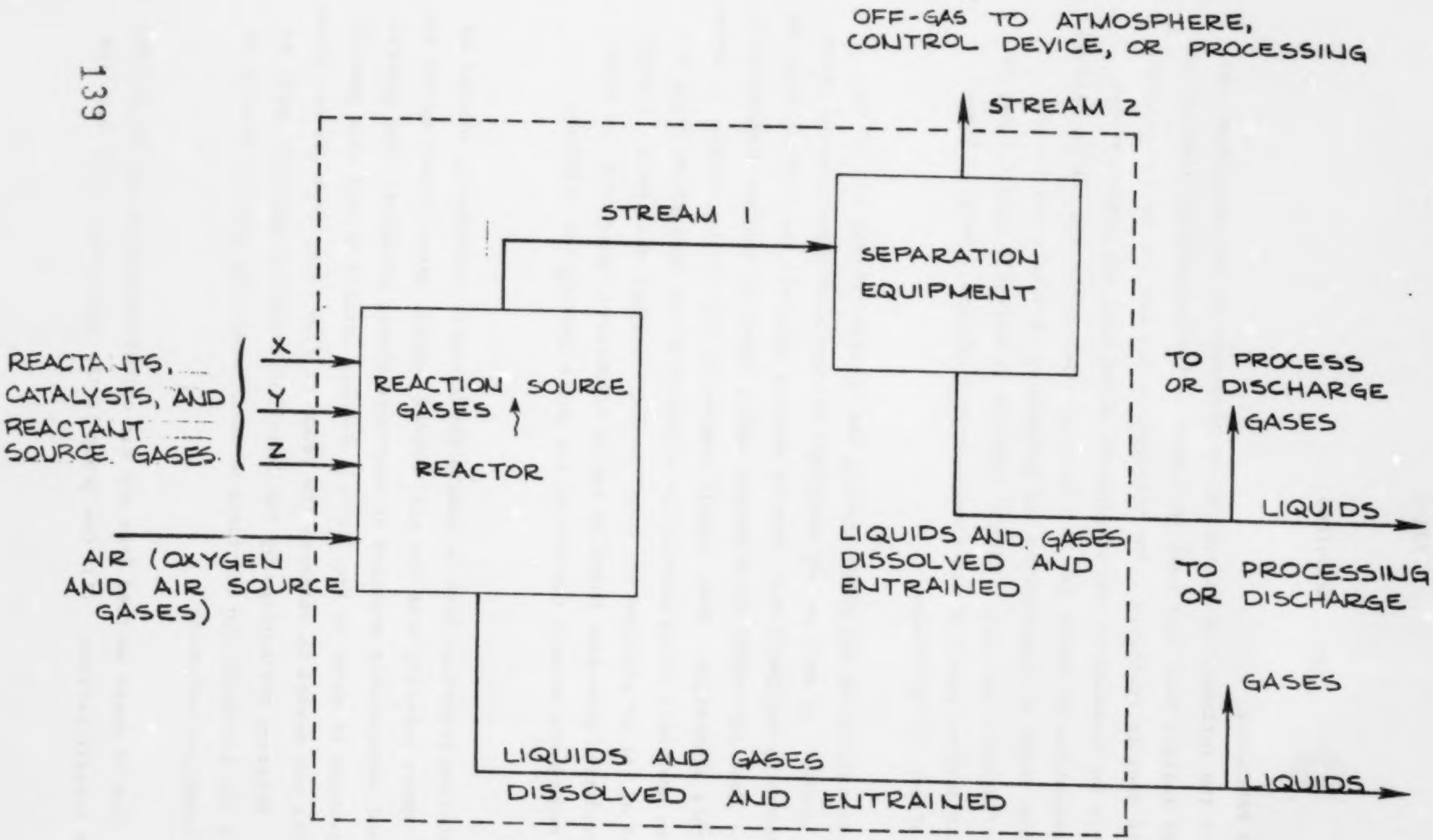

OFF-GAS TO ATMOSPHERE, CONTROL DEVICE, OR PROCESSING
STREAM 2
STREAM 1
SEPARATION EQUIPMENT
REACTANTS, CATALYSTS, AND REACTANT SOURCE GASES
X
Y
Z
REACTION SOURCE GASES
REACTOR
AIR (OXYGEN AND AIR SOURCE GASES)
TO PROCESS OR DISCHARGE
GASES
LIQUIDS
LIQUIDS AND GASES DISSOLVED AND ENTRAINED
TO PROCESSING OR DISCHARGE
GASES
LIQUIDS AND GASES
DISSOLVED AND ENTRAINED
LIQUIDS

Fig. III-1. General Air-Oxidation Process

air required for oxidation. Air is assumed to contain 21 mole % O_2 and 79 mole % N_2 (trace gases are included with the N_2). Some or all of the oxygen is consumed in the reaction; then the excess oxygen and all the nonreacted gases leave in the reactor offgas (stream 1, Fig. III-1). For convenience these gases are called air-carrier gases. (2) Organics entering the reactor as reactants may contain reaction inert materials that may also exit with the reactor off-gas (stream 1) and are called reactant-carrier gases. (3) Gases may be formed during the oxidation reaction as inorganic or organic by-products. These gases (CO, CO_2, H_2O, and others) must also leave with the reactor off-gas (stream 1) and are called oxidation reaction-carrier gases. Depending on solubilities, pressures, temperatures, and the specific materials present, some of the nitrogen and other gases may leave the reactor system with liquid streams as soluble or entrained gases. In this study it is assumed that the quantity of these soluble or entrained gases is relatively small. (Ultimately, these liquid-soluble gases appear as an emission from some other part of the process.)

The reactor off-gas (stream 1) enters the separation equipment. Condensers and other processing equipment may be used instead of, or in conjunction with, absorbers. Soluble or entrained gases leaving with the liquid stream are assumed to be relatively small. For a base case it is assumed that the air-oxidation process off-gas (stream 2) is emitted from an aqueous absorber discharging at 1.5 psig and 100°F and that it is saturated with water vapor. The total flow of this gaseous stream, S_2, is equal to the air-carrier gases not removed by the separation equipment, A; plus the reaction-carrier gases not removed by the separation equipment, R; plus the oxidation reaction-carrier gases not removed by the separation equipment, O; plus the water to saturate the gases at 100°F, W. This is expressed in the following equation:

$$S_2 = A + R + O + W \quad , \tag{1}$$

where

A = the air-carrier gases not removed by the separation equipment,

R = the reaction-carrier gases not removed by the separation equipment,

O = the oxidation reaction-carrier gases not removed by the separation equipment,

W = the water to saturate the gases at 100°F.

The gas stream (predominately N_2) at 100°F will contain 5.97 mole % water at saturation:

$$W = 0.0597\ S_2\ \text{(lb-mole/hr)}\quad . \tag{2}$$

The total off-gas stream, S_2, may also be represented by the equation

$$S_2 = G + VOC + 0.0597\ S_2\quad , \tag{3}$$

where

G = the total inorganic content of S_2 (lb-moles/hr) (inorganic carrier gases from air-carrier gases, reactant-carrier gases, and oxidation reaction-carrier gases not removed by the separation equipment),

VOC = the total organic content of S_2 (lb mole/hr) (organic carrier gases from reactant-carrier gases, and oxidation reaction-carrier gases not removed by the separation equipment).

Three major factors define the flow of air-carrier gases: the chemical oxidation reaction stoichiometry, the quantity of product produced, and the quantity of excess air fed to the reactor, which is dependent on the process operation design specific to each plant.

1. Chemical Oxidation Reaction Stoichiometry

The chemical oxidation reaction stoichiometry of the processes studied identifies four common molar oxygen ratios (MOR). The four common molar ratios (moles of O_2 reacted per mole of product produced) are listed on Table III-1.

Oxidation reactions are possible with MORs of 3/4, 5/2, 9/4, 11/4, and others. Reactions where two or more products are generated may have total MORs varying as the selectivity varies. For example, the reaction producing 50 mole % cyclohexanol and 50 mole % cyclohexanone from cyclohexane would show an overall MOR of 3/4 even though the cyclohexanone reaction has an MOR of 1 and the cyclohexanol reaction has an MOR of 1/2. The MOR is easily determined for every product to be regulated. The data base for this study has been developed to cover all products with MORs ranging from 1/2 to 9/2.

Table III-1. Common Molar Oxygen Ratios for Oxidation Processes

MOR	Products	Reactants
1/2	Acetaldehyde	Methanol
	Acetic acid	Acetaldehyde
	Cyclohexanol*	Cyclohexane
1	Cyclohexanone*	Cyclohexane
	Acrolein	Propylene
3/2	Acrylonitrile	Propylene + ammonia
	Acrylic acid	Propylene
9/2	Maleic anhydride	Benzene
	Phthalic anhydride	Naphthalene

*Co-products of cyclohexane oxidation.

2. Quantity of Product Produced

The quantity of product produced varies widely from plant to plant. A review of the information available identified a total of 158 air-oxidation plants producing 27 different chemicals with molecular weights ranging from 30 to 194. The average plant capacity was 222 $\bar{M}$ lb/yr, with capacities ranging from 6 to 1300 $\bar{M}$ lb/yr. These ranges were used to develop the data base for this study.

3. Excess Air to the Reactor

The third major consideration in defining the flow of air-carrier gases is the amount of excess air fed to the reactor. This is controlled by the specific plant operations design. The factors commonly considered when establishing the amount of excess air to be fed to the reactor include consideration of the flammable or explosive range, chemical conversion efficiencies, and product or by-product selectivity. The actual air flow data shown in Table III-2 resulted from analysis of available data from 25 specific air oxidation plants.[1]

As shown by Table III-2 the reactor air feed may be as high as 709% of theoretical. In those cases where there is less than 100% theoretical air, some oxygen must be supplied from another source, such as a chemical oxidant, or an error is indicated. The inconsistency could result from an error in the emission data reported, a variance between the estimated and actual production rate, the

Table III-2. Air-to-Reactant Relationships for Air Oxidation Processes

(A) Product	(B) Reactant	(C) MOR[a]	(D) Stoichio-metric Molar Air Flow Ratio[b]	(E) Actual Molar Air Flow Ratio[c]	(F) Percent of Theoretical Air[d]	(G) Flammable Limits (moles of air per mole of reactant)		(H) Flammable Classification		
						LEL	UEL	Above UEL	In Range	Below LEL
Acetaldehyde	Ethylene	1/2	2.38	2.62	110	37.0	2.78	X		
Acetaldehyde	Ethylene	1/2	2.38	2.57	108	37.0	2.78	X		
Acetaldehyde	Ethylene	1/2	2.38	3.01	127	37.0	2.78		X	
Acetic acid	Acetaldehyde	1/2	2.38	2.87	121	25.0	16.7	X		
Acrylonitrile	Propylene(+NH_3)	3/2	7.14	16.3	228	50.0	9.01		X	
Acrylic acid	Propylene	3/2	7.14	15.4	216	50.0	9.01		X	
Cyclohexanol	Cyclohexane	1/2-1	2.38	3.21	135	76.9	12.5	X		
Cyclohexanone			4.76	7.31	77.9[e]					
Cyclohexanol	Cyclohexane	1/2-1	2.38	2.89	121	76.9	12.5	X		
Cyclohexanone			4.76	3.39	71.2[e]					
Maleic anhydride	Butane	7/2	16.66	93.3	709	55.6	8.4			X
Maleic anhydride	Benzene	9/2	21.43	132	615	76.9	14.1			X
Acrylic acid	Propylene	3/2	7.14	14.02	196	50.0	9.01		X	
Ethylene dichloride	Ethylene	1/2	2.38	4.75	200	37.0	2.78		X	
Ethylene dichloride	Ethylene	1/2	2.38	1.72	72.3	37.0	2.78	X		
Ethylene dichloride	Ethylene	1/2	2.38	4.70	198	37.0	2.78		X	
Ethylene dichloride	Ethylene	1/2	2.38	4.72	198	37.0	2.78		X	
Ethylene dichloride	Ethylene	1/2	2.38	4.73	199	37.0	2.78		X	
Ethylene dichloride	Ethylene	1/2	2.38	1.59	66.8	37.0	2.78	X		
Acetic acid	Acetaldehyde	1/2	2.38	2.73	115	25.0	16.7	X		
Cyclohexanol	Cyclohexane	1/2-1	2.38	3.14	132	76.9	12.5	X		
Cyclohexanone			4.76	3.64	76.5[e]					
Formaldehyde	Methanol	1/2	2.38	1.73	72.7	14.9	2.78	X		
Formaldehyde	Methanol	1/2	2.38	16.86	708	14.9	2.78			X
Formaldehyde	Methanol	1/2	2.38	4.31	181	14.9	2.78		X	
Formaldehyde	Methanol	1/2	2.38	1.69	71.0	14.9	2.78	X		
Ethylene oxide	Ethylene	1/2	2.38	10.06	423	37.0	2.78		X	
Cyclohexanol	Cyclohexane	1/2-1	2.38	0.83	34.9	76.9	12.5	X		
Cyclohexanone			4.76	1.33	27.9[e,f]					

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[a] Moles of O_2 reacted per mole of product produced.

[b] Assumes 4.76 moles of air per mole of O_2 (Col C X 4.76).

[c] Calculated from actual reported reactor emission data; see ref 1.

[d] Actual air flow vs stoichiometric air flow [100 (Col E + Col D)].

[e] Reflects the selectivity of co-products cyclohexanol, cyclohexanone; average value used for calculations.

[f] Process uses HNO_3 as a chemical oxidant; excess air requirements significantly less than theoretical.

assumption that stoichiometric conditions exist when calculating the air fed to the reactor from emission off-gas data, or variances in the reaction conversion. These errors are not particularly important since the purpose of this approach is the development of a flow range and not of a specific value.

Table III-2 also lists the lower explosive limit (LEL) and upper explosive limit (UEL) for each reactant and the apparent operating position of each reaction in relation to these explosion limits. Analysis of the available data indicates that 46% of the processes operate organic-rich (above the upper limit), 13% operate organic-lean (below the lower limit), and 42% appear to operate in the flammable or explosive range. Through the use of process variations, such as back-mix reactors (fluidized bed, gas stream recycle), compounds added to modify the flammable range, and sophisticated heat transfer systems, the processes indicated to be used in the flammable range may not actually be operated in the flammable range and the risk of explosion may be remote. To establish the bases for design and costing for this study the range of theoretical air in excess of 700% was used. Very few of the air-oxidation processes being used today require theoretical air near 700%. Therefore, by setting this amount as a limit, the flow-rate range developed should include nearly every air-oxidation process in operation.

4. Total Off-Gas Flow

The total quantity of air-source gases in lb-moles/hr, A, may be expressed by the following equation:

$$A = \frac{4.76 \text{ lb-moles of air}}{\text{lb-mole of } O_2} \times \frac{CAP}{MW_p} \times MOR \times F \, , \tag{4}$$

where

CAP = plant capacity (lb/hr),

MW_p = product molecular weight (lb/lb-mole of product),

MOR = stoichiometric molar oxygen ratio (lb-moles of O_2/lb-mole of product),

F = ratio of actual air to reactor/theoretical stoichiometric air requirement.

Except for specific identifiable reactions the total reactor off-gas can best be estimated through knowledge of the excess air feed to the reactor. Within the accuracy of the design and cost projections possible for this study of air-oxidation reactions, the percent of theoretical air listed in Table III-2, column F, is the best factor for calculating the total reactor off-gas. By allowing the factor F to apply to all non-VOC off-gas emissions (water vapor from the scrubber, air-carrier gases, reactant-carrier gases, and oxidation reaction-carrier gases), the total reactor off-gas (lb-moles/hr) for oxidation reactions can be estimated by Eq. (4) as follows:

$$\text{total reactor off-gas} = \frac{4.76 \text{ lb-moles of air}}{\text{lb-mole of } O_2} \text{ X } \frac{CAP}{MW_p} \text{ X MOR X F} \quad . \qquad (5)$$

The F-factor ratio is not signficantly different when calculated as "actual air to reactor/theoretical stoichiometric air required" or as "total off-gas from reactor/ theoretical off-gas from stoichiometric air requirement". Therefore the total offgas flow for control device design can be projected by knowledge of the F ratio determined by either means, the molecular weight of the product produced, and the plant production rate.

The F-ratio has been correlated with several physical parameters in vapor-phase air oxidations. Important variables in this correlation are the average reactor temperature, the autoignition temperature of the feedstock, and the explosive limits of the feedstock mixture. Although the level of precision related to the use of this mathematical correlation is not necessary to estimate the flow-rate range for the purpose of this report, it may be useful in developing more accurate predictions of flow from air-oxidation processes.[2]

The total off-gas flow rate projection for air oxidation processes, Fig. III-2, was formed by using Eq. (5) and the data from Table III-2 plus actual plant data available from the production of 28 air-oxidation products (see Appendix A). A family of total off-gas index curves [combining MOR and F from Eq. (5)] is plotted on Fig. III-2 to facilitate the projection of off-gas flow rates for the full range of product molecular weights and plant capacities. The flow rates have been converted to a plant capacity of scfm* per million pounds a

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*Standard conditions used throughout this report are 32°F and 760 mm Hg.

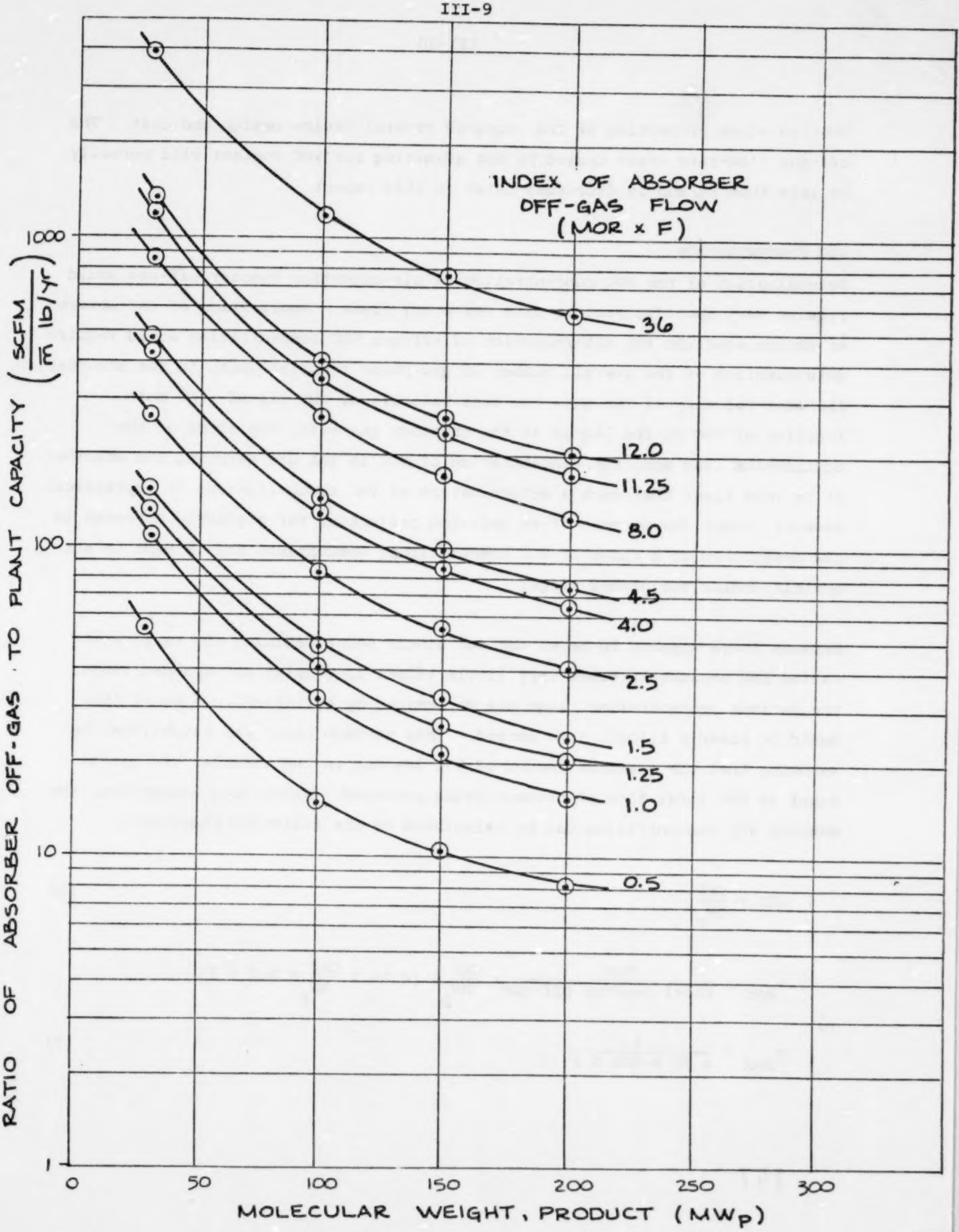

Fig. III-2. Total Off-Gas Flow-Rate Projection for Air-Oxidation Processes

year to allow projection of the required control device design and cost. The off-gas flow-rate error caused by not adjusting for VOC content will normally be less than 2% and is discussed later in this report.

C. VOC CONCENTRATION

Determination of the VOC concentration of air-oxidation reactor off-gas would require very specific process data for every plant. Application of the absorber design equation for determination of off-gas VOC concentration would require determination of the overall number of gas-phase transfer units in the absorber, the mass velocity of the gas, the mass velocity of the liquid, the mole fraction of VOC in the liquid at the absorber gas exit, the slope of the equilibrium line and, the concentration of VOC in the gas entering the absorber. It is very clear that such a determination of VOC concentrations is impractical. However, since the purpose of an emission projection for a generic approach is the definition of a range of VOC compositions, assumptions may be made to adequately define the needed range.

Because there appears to be no obvious single point defining the range limitation and because it takes very little effort to display an expanded range, the maximum concentration range was determined by establishing a point that would be clearly illogical to exceed. This maximum point was established by assuming that the greatest amount of VOC leaving in the scrubber off-gas is equal to the total flow of product being produced. Given this assumption, the maximum VOC concentration can be calculated by the following equations:

$$\text{VOC} = \frac{\text{CAP}}{\text{MW}_p} , \qquad (6)$$

$$Y_{max} = \frac{\text{VOC}}{\text{total reactor off-gas}} = \frac{\text{CAP}}{\text{MW}_p} \div \left(4.76 \text{ X } \frac{\text{CAP}}{\text{MW}_p} \text{ X MOR X F}\right) ,$$

or

$$Y_{max} = \frac{1}{4.76 \text{ X MOR X F}} , \qquad (7)$$

where

VOC = total VOC in off-gas (lb-moles/hr),

CAP = plant capacity (lb/hr),

MW_p = product molecular weight (lb/lb-mole of product),

Y_{max} = maximum VOC concentration (mole fraction),

Total reactor off-gas - [see Eq. (5)] where it is assumed that:

4.76 lb mole air/lb-mole of O_2 and

MOR X F = total absorber off-gas flow index.

A comparison of projected maximum VOC concentrations to actual VOC concentrations available for this study is shown by Table III-3. The actual VOC concentrations are also displayed by the histogram of Fig. III-3. The actual plant data currently available for 11 plants show all off-gas emissions to contain less than 5% VOC.[1]

The full range of the index of absorber off-gas flow (MOR X F) used for the total off-gas flow-rate projections shown by Fig. III-2 has been used to calculate the maximum potential VOC concentrations shown on Fig. III-4.

The significant conclusions from Fig. III-4 that affect thermal oxidation design, size, and cost are that (1) any off-gas with a flow index (MOR X F) greater than 2 must have a VOC concentration of less than 10 mole %, (2) quantitative verification is provided to show that only relatively low off-gas flows can have VOC concentrations greater than 10 mole %, and (3) the highest off-gas VOC concentration observed from limited available data is less than 5 mole %.

Since the maximum VOC concentration indicated by Fig. III-4 is based on the unrealistic assumption that all product might be emitted as off-gas, actual VOC concentrations will normally be considerably lower.

Table III-3. Air Oxidation Absorber Off-Gas VOC Compositions[a]

Actual VOC Composition Range (mole %)	Products	Actual VOC Composition (mole %)	Maximum VOC Composition[b] (mole %)
Less than 0.1	Acetic acid	0.002	37
	Acetaldehyde	0.03	39
	Acetaldehyde	0.036	38
	Formaldehyde	0.049	58
0.1 - 0.499	Acetaldehyde	0.17	33
	Acetic acid	0.21	35
	Cyclohexanol/cyclohexanone	0.26	20 - 40[c]
	Cyclohexanol/cyclohexanone	0.34	20 - 40[c]
	Maleic anhydride	0.40	0.85
	Cyclohexanol/cyclohexanone	0.498	20 - 40[c]
0.5 - 0.999	Formaldehyde	0.54	5.9 - 23[d]
	Ethylene dichloride	0.80	63
	Acrylonitrile	0.81	6.1
1.0 - 1.999	Ethylene dichloride	1.05	34
	Acrylic acid	1.39	7.2
	Ethylene dichloride	1.90	50
2.0 and greater	Ethylene dichloride	2.52	58

[a] See ref 1.

[b] Calculated by Eq. (7).

[c] Depending on product mix.

[d] Depending on degree of off-gas recycle.

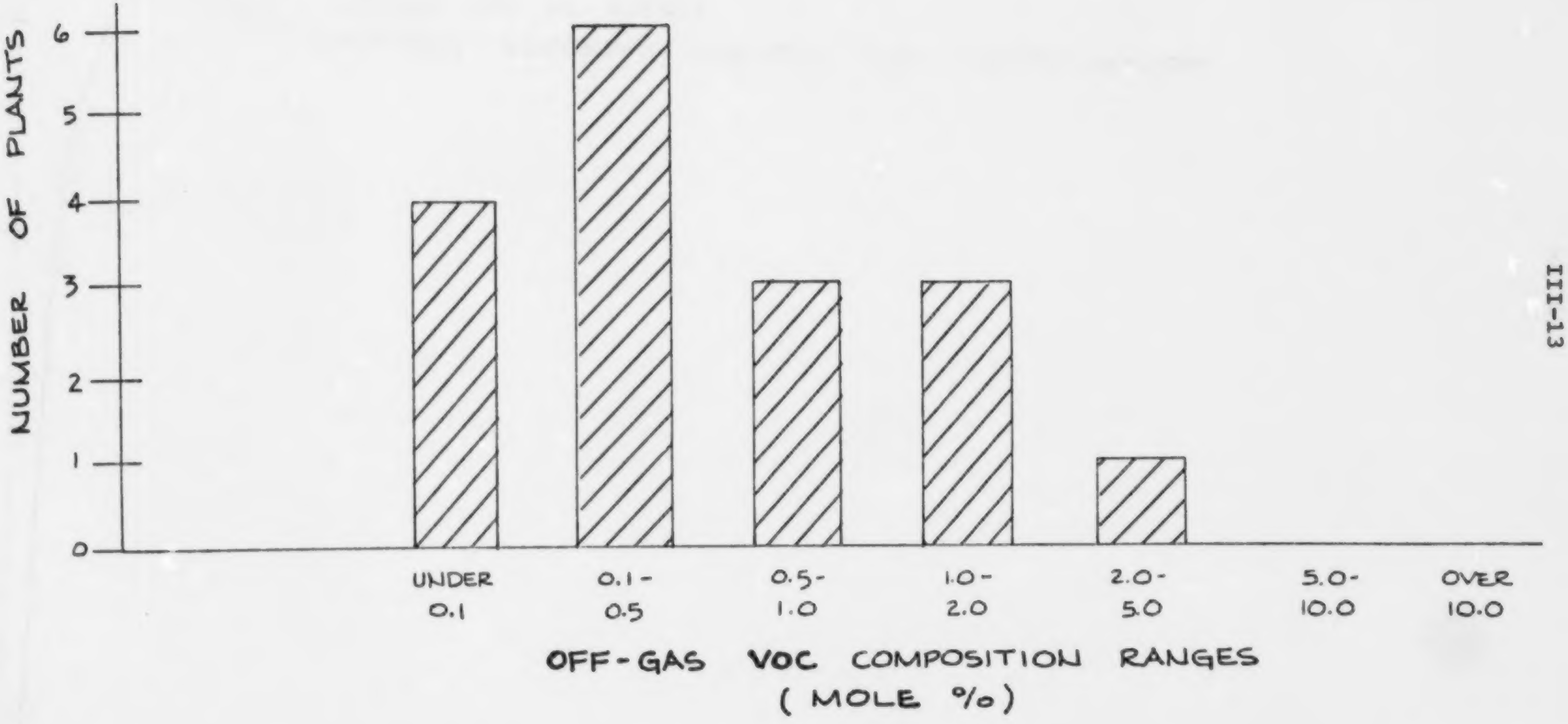

Fig. III-3. Distribution of Actual Absorber Off-Gas VOC Composition Data Found in HI Study

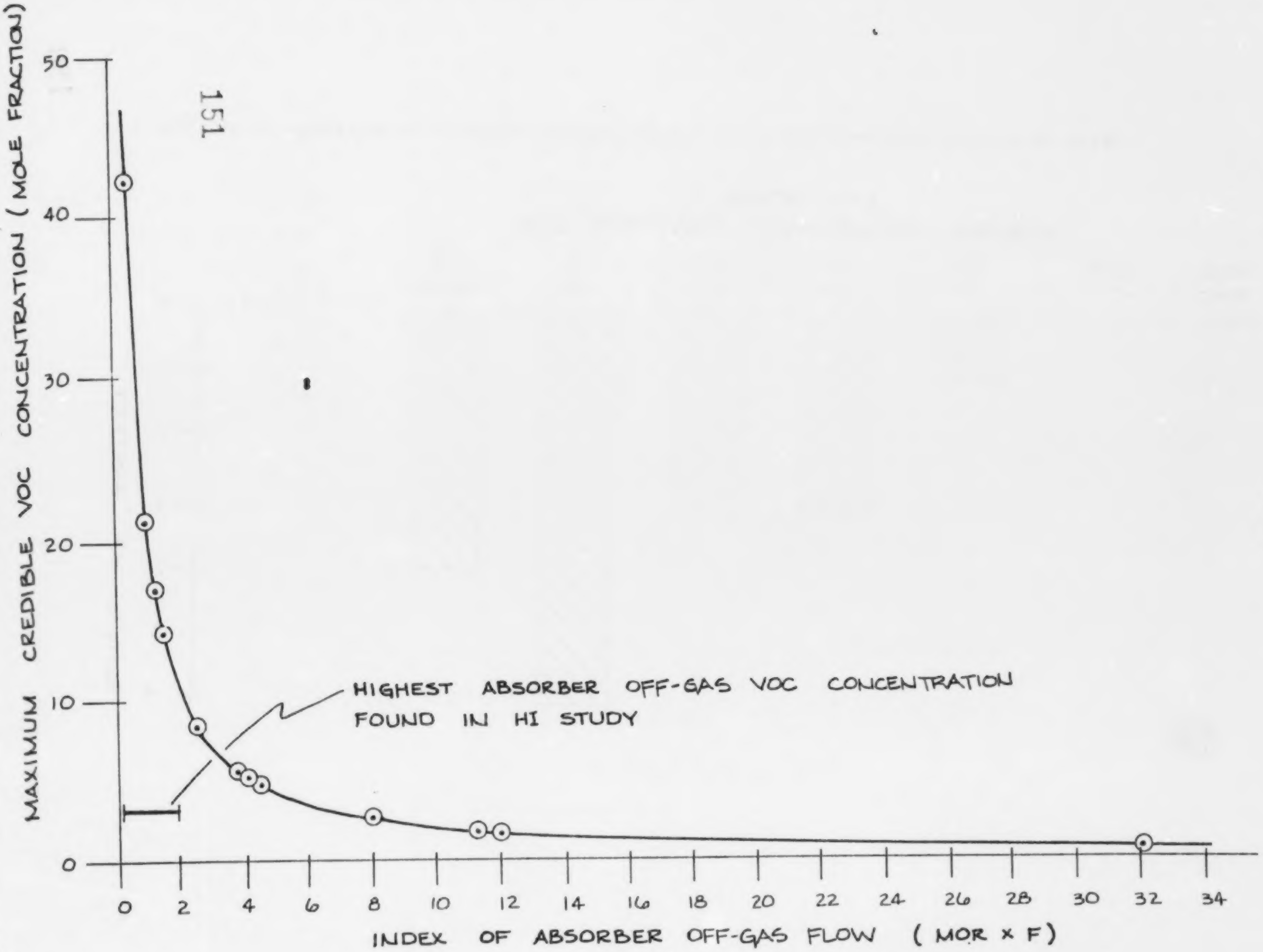

Fig. III-4. Maximum Off-Gas VOC Concentration as a Function of Off-Gas Flow Index Factor

D. REFERENCE*

1. Site visits and letters received by EPA describing processes and emissions. See Appendix A for a list of information sources.

2. A. Miles and B. Newman, "Statistical Analysis and Industry Profile," Energy and Environmental Analysis draft report to the EPA, October 1979.

*When a reference number is used at the end of a paragraph or on a heading, it usually refers to the entire paragraph or material under the heading. When, however, an additional reference is required for only a certain portion of the paragraph or captioned material, the earlier reference number may not apply to that particular portion.

IV. CONTROL OPTIONS

A variety of control devices for organic emissions were reported on in control device evaluation reports. These reports discuss the limitations of each control device and offer costs as functions of the applicable flow and composition ranges for each device. Table IV-1 summarizes the cost-effectiveness for each control technology for a typical case. This table should only be used to identify the most cost-effective technologies in a general way since other considerations may cause the costs to change. When a control technology is selected, the control device evaluation reports may be used to more completely identify the costs.

Air oxidation processes generate waste gases at flows from under 1000 scfm to 100,000 scfm and are typically dilute in VOC (the highest composition found in this study was about 2 vol %). Air oxidation processes would therefore span the flow range presented in Table IV-1 and be in the low and medium concentration catagories. Therefore, technologies appropriate for control of air oxidation processes are condensation, absorption, adsorption, catalytic oxidation, thermal oxidation, and high temperature oxidation.

Condensation is most appropriate for waste gases of flows under 5000 scfm. It is only effective where the VOC present is condensible or in other words, not an organic carrier gas. Since in air oxidation processes reactants and products must be separated from the waste gas, it is likely that if condensation is effective in reducing organic losses, it has already been utilized in the process. Further information on condensation is available in the control device evaluation on condensation.

Absorption is also a technology which would be expected to exist today in air oxidation plants. In fact, aqueous absorption is assumed to be present in the process prior to generation of the waste gas. Although in some cases adding additional absorption equipment may be possible, it is unlikely that organic removals above that achieved by the existing equipment could approach 90%. Absorption is also discussed in more detail in a control device evaluation report.

Table IV-1. Representative Cost-Effectiveness for Organic Emission Control Technology

Waste Gas Flow (scfm)	VOC Concentration[a]	Cost Effectiveness (per lb of VOC) for						
		Condensation[b]	Absorption[c]	Adsorption[d]	Flares[e]	Catalytic Oxidation[f]	Thermal Oxidation[g]	High-Temperature Oxidation[h]
500—700	Low	$0.20	i	i	j	$0.31—0.37	$0.55—0.62	$0.78—1.29
	Medium	0.03	i	i	j	k	0.09—0.11	0.20—0.30
	High	0.06	i	i	i	k	0.06	0.12—0.17
1000	Low	0.14	$0.56—1.07	$0.13—0.15	j	i	i	i
	Medium	0.02	0.06—0.11	k	j	k	i	i
	High	0.04	i	k	$0.001	k	i	i
5,000	Low	l	0.20—0.55	0.06—0.08	j	0.09—0.12	0.25—0.29	0.44—0.78
	Medium	l	0.04—0.08	k	j	k	0.02—0.04	0.13—0.19
	High	l	i	k	i	k	0.01	0.09—0.12
50,000	Low	l	0.02—0.18	0.03—0.05	j	0.05—0.07	0.20—0.24	0.37
	Medium	l	0.10—0.45	k	j	k	0.01—0.02	0.11
	High	l	i	k	i	k	0.007	0.08

[a] Low ≅ 0.5 vol % or 10 Btu/scf; medium ≅ 5 vol % or 50 Btu/scf; high ≅ 20 vol % or 100 Btu/scf.

[b] 95% removal efficiency; no VOC credit.

[c] 99% removal efficiency; $L_m/mG_m = 1.4$; steam ratio = 0.2 moles of steam/mole of waste gas; no VOC credit.

[d] 70—12 ppm effluent; 6.96 lb of carbon/1000 scf; no VOC credit; loading - 0.1 lb of VOC/lb of carbon, molecular weight of VOC = 50.

[e] Based on 100% VOC of propylene at 100% of capacity. Flares normally operate intermittently at a low fraction of capacity.

[f] 90—90% destruction efficiency; no heat recovery.

[g] 90—99% destruction efficiency; no heat recovery, 1400—1600°F combustion temperature..

[h] 99.9% destruction efficiency; no heat recovery, 2200—2600°F combustion temperature.

[i] Costs not available.

[j] Not applicable at low concentrations.

[k] Not applicable at high concentrations.

[l] Not applicable at high flow rates.

Carbon adsorption can only be applied at low-VOC concentrations. It compares attractively to all control technologies on a cost-effectiveness basis. However, in addition to its concentration limitations, carbon adsorption is not effective on a number of organic compounds. Where it is applicable carbon adsorption is expected to be highly cost-effective. A control device evaluation report on adsorption more completely defines its limitations.

Catalytic oxidation is only applicable for low VOC concentration waste gases as long as catalyst poisons aren't present. Catalytic oxidation can be more cost effective than thermal oxidation if it can be applied to the waste gas. Further information on catalytic oxidation may be found in the control device evaluation report on catalytic oxidation.

Thermal oxidation applies to the flow range and concentration range of waste gases from an oxidation process. In addition, all organic compounds can be oxidized in thermal oxidation units. However, thermal oxidizers do utilize significant quantities of fuel when burning low-concentration waste gases. Thermal oxidation is discussed in the thermal oxidation control device evaluation.

When compounds containing sulfur or other particular elements are present in the waste gas, noxious compounds are emitted in the flue gas. Scrubbers are then required to remove the noxious gases from the flue gas prior to discharge. When chlorine-containing compounds are present, the combustion temperature must be increased to convert the Cl to HCl instead of Cl_2. This aids the removal of chlorine from the flue gas. These special cases of thermal oxidation are discussed in the thermal oxidation supplementary control device evaluation.

V. SUMMARY

Air-oxidation processes are major contributers of organic emissions. A method of estimating the range of flow and VOC concentration from air-oxidation processes has been developed.

Control technologies technically applicable to air-oxidation organic emissions are thermal oxidation, high-temperature thermal oxidation, catalytic oxidation, and carbon adsorption. Condensation and absorption are assumed to be part of the process. More detailed discussions of the technical and economic considerations of these control devices can be found in the Control Device Evaluation reports on each of these technologies. Economic, environmental, and energy inpacts of control of air-oxidation organic emissions can be developed over the flow and VOC concentration ranges as established in this report.

APPENDIX A

LIST OF EPA INFORMATION SOURCES

1. J. J. Cudahy and J. F. Lawson, IT Enviroscience, Inc., Trip Report on Visit Regarding Longview, TX, Plant of Texas Eastman, Nov. 16, 1977 (on file at EPA, ESED, Research Triangle Park, NC).

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REPORT 4

VACUUM SYSTEM EMISSION PROJECTIONS

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Office of Air Quality Planning and Standards
ENVIRONMENTAL PROTECTION AGENCY
Research Triangle Park, North Carolina

December 1980

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I. THE GENERIC STANDARD APPROACH

For a discussion of the basis for the generic standard concept see the report in this volume entitled "The Generic Standard Approach." The reader is advised to read this report since the concept and essential terminology is explained therein. This report is an overview of the potential organic emissions from vacuum systems in SOCMI and was based only on existing data collected during the beginning of the IT Enviroscience study. This report has served as the basis of further work by other EPA contractors. Their work will improve the available data base on vacuum systems and provide additional detail as may be needed to form the basis for preparation of the standards.

II. VACUUM SYSTEMS IN THE SYNTHETIC ORGANIC CHEMICALS MANUFACTURING INDUSTRY

A. MAJOR USES OF VACUUM

Vacuum processes in the chemical industry relate to any processes operated at pressures below atmospheric pressure (760 mm Hg). In reality, most vacuum processes (such as solvent distillation) are performed at pressures greater than 1 mm Hg although in some special cases, such as molecular distillation, pressures as low as 0.01 mm Hg can be involved.

1. Advantages of Using Vacuum

Processes operated under vacuum have three advantages compared to their atmospheric or elevated pressure counterparts. These advantages are associated with thermal effects, fluid-transfer effects, or special effects.

a. Thermal Effects of Vacuum—Advantages related to thermal vacuum effects arise from the chemical exerting a higher partial pressure under reduced pressure (vacuum) than at atmospheric or elevated pressures (with the temperatures assumed to be the same). Consequently the boiling point of the liquid is lowered (compared to that at atmospheric pressure). This approach has utility when the liquid or a component in the liquid is highly reactive or is prone to decomposition. Undesirable reactions and decompositions are often related to temperature, and therefore processes operating at lower temperatures (because of vacuum) have much less product loss to undesirable by-products.

Compounds for which vacuum processing is used to forestall undesirable side reactions or decomposition include high-molecular-weight alkenes, aldehydes, carboxylic acids, alcohols, and other compounds with reactive functional groups.

Vacuum is also used to modify the operating conditions so that lower grade heat sources (such as 150-psi steam) can be used.

b. Fluid Transfer Effects of Vacuum—Fluids flow from higher pressures to lower pressures. Vacuum generates the low pressure into which liquids, gases, and slurries can flow. This approach is used in those simple cases where the objective is to transfer liquids from one vessel to another without the use of liquid pumps, since the mechanical shear generated in pumps can be deleterious to process chemicals. More complicated applications of vacuum for fluid flow include vacuum filtration. In those cases liquid-solid slurries flow to the filter media surface, where the solids remain and form a cake and the liquids pass through. The liquid flow is induced by atmospheric pressure pushing the liquid in the direction of the vacuum.

c. Special Effects of Vacuum---Vacuum is sometimes used in reactions or separations to achieve yields or separation efficiencies between components, which are difficult or impossible to achieve at atmospheric or elevated pressures. This often results in beneficial changes in physical properties at reduced pressures. For instance, compounds with very similar vapor pressures at atmospheric pressure but with divergent vapor pressures at reduced pressures may easily be separated by distillation under vacuum, whereas distillation at atmospheric pressure would be difficult.

2. Types of Vacuum Processes

Nearly any type of chemical process vessel may be designed to operate under vacuum. These vessels are categorized as reactors, absorbers, distillation units, crystallizers, and filters.

a. Vacuum Reactors---Reactors are placed under vacuum primarily to take advantage of the different thermal characteristics of the chemicals being handled, although sometimes special vacuum effects are important. Lowered boiling points allow chemicals to be removed by vaporization during the reaction, thus improving conversion and decreasing undesirable side reactions and decomposition of sensitive chemicals. Reducing the pressure can also affect conversions by shifting reaction rates to favor the products desired. Some reactors operate at reduced pressure to increase the selectivities or to improve reaction yields. Physical property changes with reduced pressure improve performance compared to that obtained at atmospheric pressure.

b. Vacuum Absorbers---Vacuum absorbers may be used after a vacuum reaction in which a component of the reaction off-gas is to be recovered by absorption. The vacuum device is usually placed at the end of the reactor-absorber train and supplies the motive force for gas flow through the absorbers.

c. Vacuum Distillation Units——Vacuum distillation units are used for reasons similar to those applying to the vacuum reactors. Thermal effects of lowered boiling points to lessen decomposition or enhanced separations because of such special effects as physical property changes are usually significant. Low-temperature vacuum distillation often provides an economic advantage by allowing the use of a lower temperature, less expensive heat supply.

d. Vacuum Crystallizers——Vacuum crystallizers often utilize the thermal effects of lowered boiling points under reduced pressure to remove solvents, which generates efficient cooling and also causes solute concentrations to increase and thereby form solids. Vacuum operation is preferred when the solids are temperature-sensitive or have low melting points or to prevent scaling of surface heat exchangers.

e. Vacuum Filters——The decision of whether to select vacuum filters or pressure filters largely depends on the filtration characteristics of the slurry being filtered and the properties of the resulting filter cake. These considerations result from actual laboratory testing and are very specific to the stream being filtered. Vacuum filtration is used widely in processing industries.

B. TYPES OF VACUUM DEVICES

Two major types of vacuum-generating devices exist: ejectors or eductors and pumps. Ejectors or eductors develop vacuum or reduced pressure when steam or liquids flow through restricted passages or venturis. Vacuum pumps utilize mechanical drives and positive-displacement actions to generate vacuums.

1. Ejectors or Eductors

The most common vacuum device used in past industrial operation is the steam ejector. Eductors are similar to ejectors except that they use liquids as the motivating fluid. Ejectors can generate pressures as low as 0.0001 mm Hg by using five or six ejector stages. The gas-handling capacity and vacuum developed by an ejector is strongly dependent on the throat diameter of the venturi and other venturi design variables. Ejectors can be designed for very large flows. For example, systems with capacities in the millions of scfm of air have been constructed in the aerospace industry. Ejectors in use in SOCMI have capacities of less than 10,000 scfm, with the majority being less than 1000 scfm.

Steam ejectors are designed with either contact or surface condensers and usually with barometric seal legs about 35 ft long. Surface-condenser systems can be designed with a condensate receiver and discharge pump in place of the barometric seals. The condensers condense the steam and any condensible vapors in the waste gas, and the barometric leg or condensate receiver seals the vacuum device from atmospheric pressure. A three-stage steam ejector system with contact condensers and a barometic seal is shown in Fig. II-1, and one with surface condensers and a condensate receiver system is shown in Fig. II-2. Surface condensers can also utilize barometric seals. Considerable water is used to condense the steam in a contact condenser system and usually becomes a wastewater or secondary emission source since it becomes contaminated with organics present in the vacuum process. Although surface condensers prevent the organic vapors from being contacted with water, thus allowing for water recycling through cooling towers, they are more expensive to install than contact condensers. Surface condensers can often be more practical and economical than contact condensers because of the possibility of recovering VOC, of the likelihood of using emission control that is more cost-effective, and of VOC not having to be separated from the cooling water.

The design of ejector systems requires information on the the following parameters:[1]* suction temperature, capacity (rate for each constituent), component information (molecular weight, vapor pressure, and water solubility of each component), evacuation requirements (system volume, leak rates, initial and final pressures, evacuation times, evaporation rates of any liquid in the system), suction pressure, motive steam temperatures and pressures, maximum discharge pressure, cooling water temperature, construction materials, condenser requirements, space limitations, and other considerations.

2. Vacuum Pumps

Vacuum pumps can be classified generally as water-sealed, oil-sealed, or gas-sealed pumps. Water-sealed pumps have the general design of a vane impeller rotating in a casing filled with water (or another process fluid). Air is captured at the pump suction and released at the pump discharge, thereby generating a reduced pressure. Oil-sealed pumps utilize a principle similar to that of water-sealed pumps except that circular, elliptical,or other complex-shaped

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*See Sect. VI for references cited in this report.

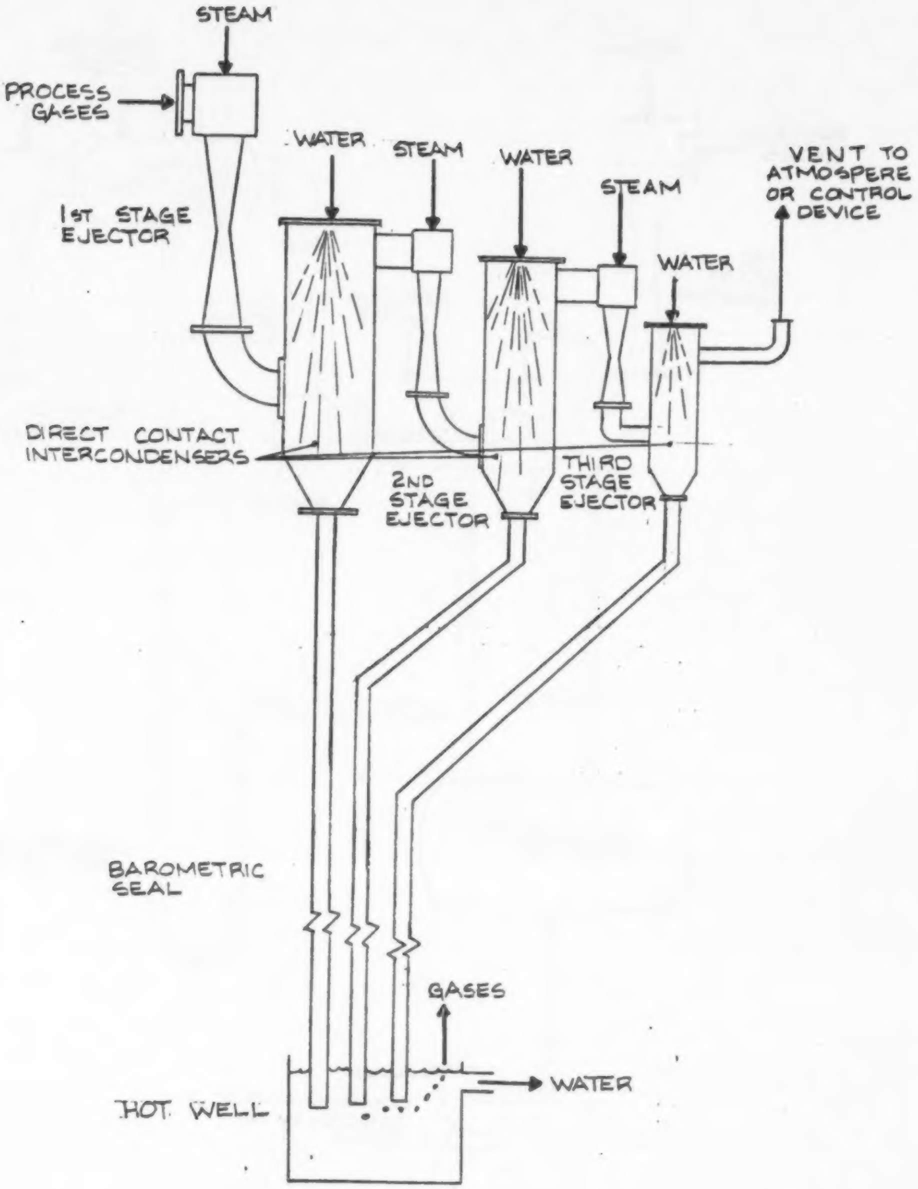

STEAM
PROCESS GASES
1ST STAGE EJECTOR
WATER
STEAM
WATER
STEAM
VENT TO ATMOSPERE OR CONTROL DEVICE
WATER
DIRECT CONTACT INTERCONDENSERS
2ND STAGE EJECTOR
THIRD STAGE EJECTOR
BAROMETRIC SEAL
GASES
WATER
HOT WELL

Fig. II-1. Three-Stage Steam Ejectors with Contact Condensers and a Barometric Seal

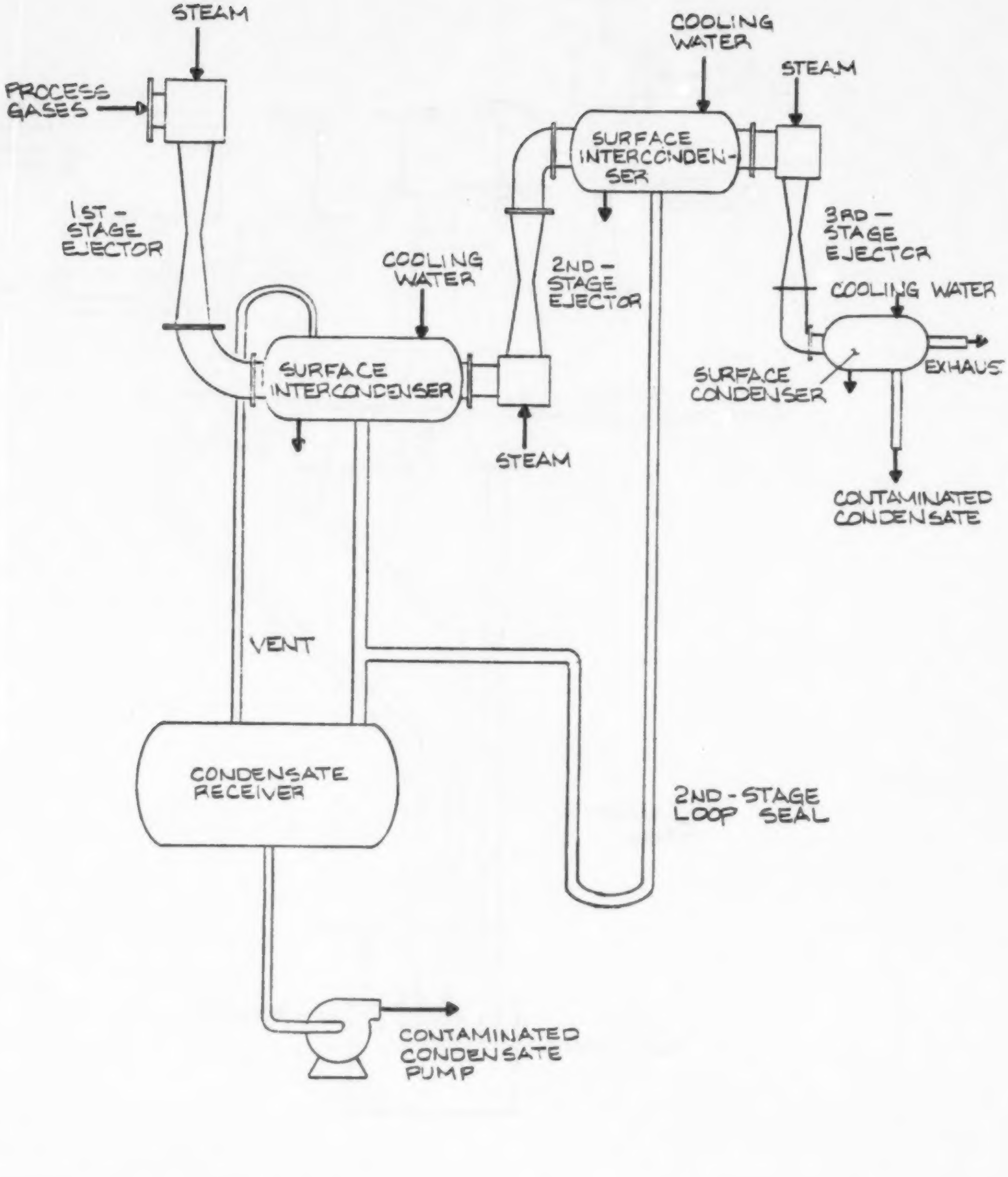

STEAM
PROCESS GASES
1ST-STAGE EJECTOR
COOLING WATER
SURFACE INTERCONDENSER
STEAM
2ND-STAGE EJECTOR
COOLING WATER
SURFACE INTERCONDENSER
STEAM
3RD-STAGE EJECTOR
COOLING WATER
SURFACE CONDENSER
EXHAUST
CONTAMINATED CONDENSATE
VENT
CONDENSATE RECEIVER
2ND-STAGE LOOP SEAL
CONTAMINATED CONDENSATE PUMP

Fig. II-2. Three-Stage Steam Ejector with Surface Condensers and a Condensate Receiver System

rotary pistons or vanes capture the air at the suction, and close oil-lubricated tolerances, instead of water seals, seal the suction from the discharge. Gas-sealed pumps (sometimes called dry pumps) use no seal liquid but depend on surfaces machined to close tolerances to achieve vacuums. Figure II-3 is a simplified diagram of some configurations of mechanical vacuum pumps.

Water-sealed vacuum pumps achieve pressures of about 150 mm Hg with single-stage design and 20 to 30 mm Hg with two-stage design. Capacities can range over 20,000 cfm. Oil-sealed pumps can achieve pressures as low as 0.0001 mm Hg, and capacities of up to 1500 cfm are available. Gas-sealed pumps have capacities of up to 6600 cfm and can develop pressures as low as 0.0001 mm Hg.[2,3]

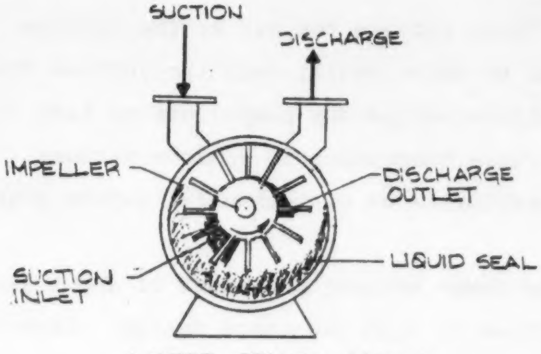
Design or detailed discussion of the vacuum sources is beyond the scope of this study. Many references are available for further discussion of steam ejector design[4—11] and vacuum pump selection and design.[12—16]

3. Usage of Vacuum Devices

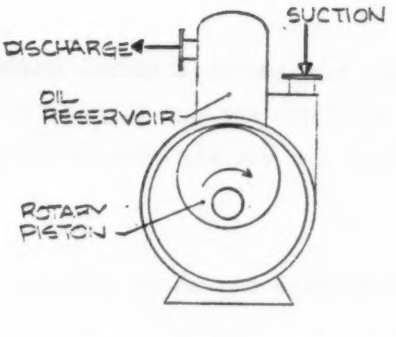
Since ejectors are commonly powered by steam, considerable energy may be consumed in maintaining the vacuum. In fact, steam ejectors are the highest energy consumers of vacuum devices. Energy efficiencies for various vacuum sources are shown in Table II-1.[17]

Table II-1. Maximum Energy Efficiencies of Vacuum Sources

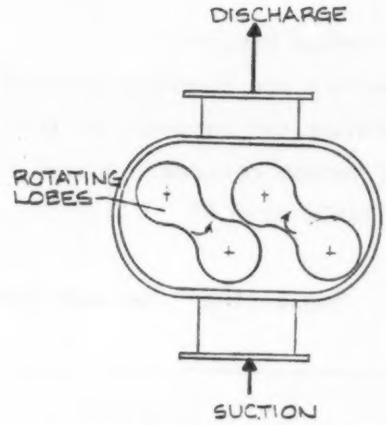
Vacuum Source	Maximum Energy Efficiency (%)	Suction Pressure at Maximum Energy Efficiency (mm Hg)
Roots type blower, gas-sealed	68	600
Rotary piston, oil-sealed	54	150
Liquid ring, water-sealed	48	300
Liquid eductor	25	300
Steam ejector	6	10


SUCTION
DISCHARGE
IMPELLER
DISCHARGE OUTLET
SUCTION INLET
LIQUID SEAL

WATER-SEALED LIQUID RING VACUUM PUMP


DISCHARGE
SUCTION
OIL RESERVOIR
ROTARY PISTON

OIL-SEALED ROTARY-PISTON VACUUM PUMP


DISCHARGE
ROTATING LOBES
SUCTION

GAS-SEALED ROOTS-TYPE BLOWER VACUUM PUMP

Fig. II-3. Some Configurations of Mechanical Vacuum Pumps

Vacuum pumps are presently being considered as replacements for many of the duties traditionally performed by steam ejectors, primarily because of their lower energy costs. The high-energy consumption of steam ejectors is leading to increased use of vacuum pumps in SOCMI. This trend is expected to continue, but steam ejectors will probably always be found in SOCMI.

C. DISTRIBUTION OF VACUUM SYSTEMS IN SOCMI

No comprehensive detailed information is available on the exact number and use of vacuum devices in SOCMI. Vacuum processes can be highly confidential to the chemical companies and will vary substantially from site to site. During the course of the IT Enviroscience study of chemical processes a significant body of information was collected on emission sources. An index of products studied by IT Enviroscience for which vacuum processes are used or believed to be used is given in Table II-2. Product reports generated by IT Enviroscience are the primary sources for this information but in some cases individuals who authored these reports suspected the use of vacuum processes even if the model plant flowsheets do not show vacuum equipment. A list of IT Enviroscience reports supporting Table II-2 are presented in the Appendix.

Figures II-4, II-5, and II-6 show examples of processes that use vacuum reactors, absorbers, distillation units, and crystallizers. No data on vacuum filtration were requested or collected in the IT Enviroscience study. It is quite possible that the filtration unit shown on some of the study flowsheets are vacuum filtration units, since this type of operation is used extensively in the industry when filtration is required.

Of the 99 distillation operations on which IT Enviroscience has data, one-third were found to be vacuum distillation units. The average VOC emission from all distillation units is about 10.7 lb/hr. But the average VOC emission from vacuum distillation units alone is about 15 lb/hr. A study on the use of vacuum distillation in petroleum refineries[18] shows that 35% of the refinery capacity is vacuum-distilled.

A variety of preliminary plant designs for 25 products and 151 processes were surveyed[19] to establish the number of vacuum distillation units and other types of vacuum systems in operation. About 11% of the reactors, 9% of the absorbers,

Table II-2. Estimated Number of Vacuum Processes in Chemical Processes Studied by Hydroscience[a]

Chemical	Number of Vacuum Systems in Use				
	Reactors	Absorbers	Distillation Units	Crystallizers	Filters
Acetic anhydride	1	3			
Acetone (see phenol)					
Acetone cyanohydrin			1		
Acrolein			1		
Acrylic acid and esters			10		
Adipic acid			2	1–5	1–5[b]
Alkylbenzene			3–4		
Caprolactam			2	1–5	1–5[b]
Chlorobenzene			3		
Chloroprene			4		
Dimethylterephthalate			2		
Ethanolamines			4		
Ethylbenzene			1		
Ethylene glycol			4		
Formaldehyde			1		
Glycerin			5		
Glycol ethers			3		
Maleic anhydride			3		
Methyl methacrylate			2		
Phenol/acetone			1–8		
Propylene oxide			3		
Styrene			3		
Sulfuric acid (recovery)			1		
Terephthalic acid			1		
Toluene diisocyanate			5		

[a] See Appendix A for references.

[b] Possible use of vacuum filters.

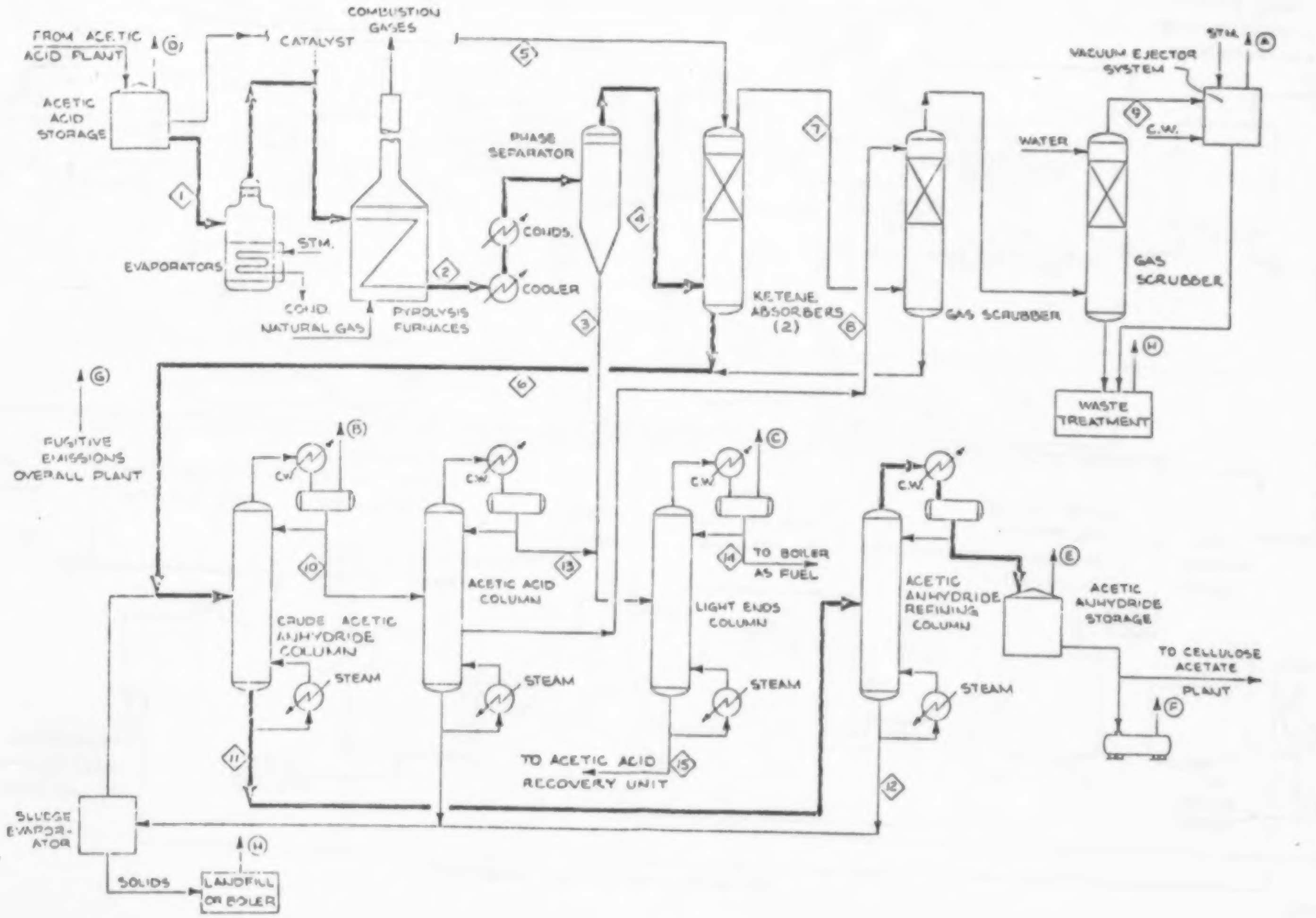

FROM ACETIC ACID PLANT
D
ACETIC ACID STORAGE
1
CATALYST
COMBUSTION GASES
EVAPORATORS
STM.
COND.
NATURAL GAS
PYROLYSIS FURNACES
2
COOLER
CONDS.
PHASE SEPARATOR
3
4
5
KETENE ABSORBERS (2)
6
7
8
GAS SCRUBBER
WATER
GAS SCRUBBER
9
C.W.
VACUUM EJECTOR SYSTEM
STM.
A
H
WASTE TREATMENT
G
FUGITIVE EMISSIONS OVERALL PLANT
C.W.
B
10
CRUDE ACETIC ANHYDRIDE COLUMN
STEAM
11
C.W.
13
ACETIC ACID COLUMN
STEAM
C.W.
C
14
TO BOILER AS FUEL
LIGHT ENDS COLUMN
STEAM
15
TO ACETIC ACID RECOVERY UNIT
C.W.
ACETIC ANHYDRIDE REFINING COLUMN
STEAM
12
E
ACETIC ANHYDRIDE STORAGE
TO CELLULOSE ACETATE PLANT
F
SLUDGE EVAPORATOR
SOLIDS
H
LANDFILL OR BOILER

Fig II-4. Flow Diagram for a Process Utilizing Vacuum Reactors and Absorbers (Acetic Anhydride)

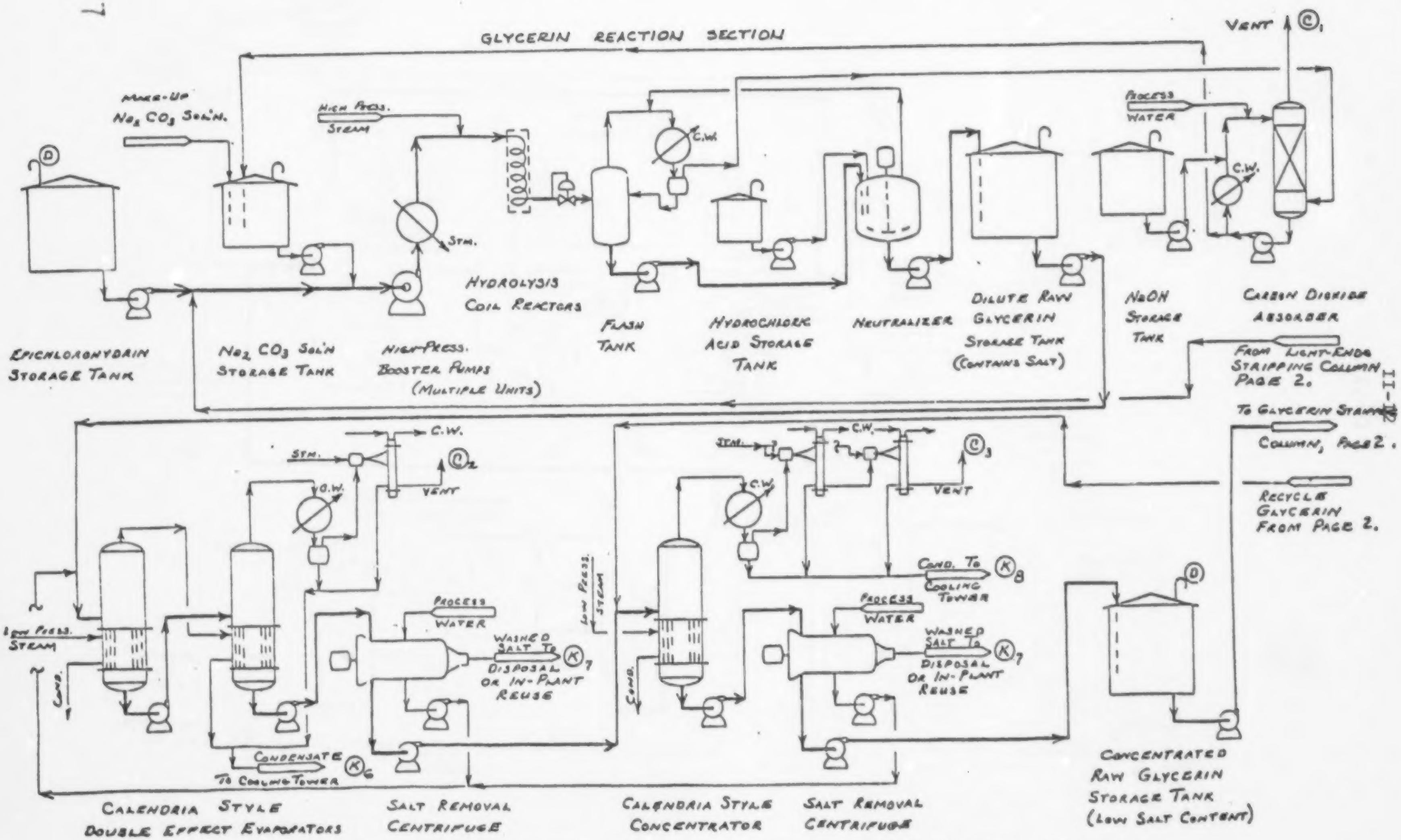

GLYCERIN REACTION SECTION
VENT
©₁
MAKE-UP Na₂ CO₃ SOL'N.
HIGH PRESS. STEAM
PROCESS WATER
C.W.
C.W.
STM.
D
EPICHLOROHYDRIN STORAGE TANK
Na₂ CO₃ SOL'N STORAGE TANK
HIGH-PRESS. BOOSTER PUMPS (MULTIPLE UNITS)
HYDROLYSIS COIL REACTORS
FLASH TANK
HYDROCHLORIC ACID STORAGE TANK
NEUTRALIZER
DILUTE RAW GLYCERIN STORAGE TANK (CONTAINS SALT)
NaOH STORAGE TANK
CARBON DIOXIDE ABSORBER
FROM LIGHT-ENDS STRIPPING COLUMN PAGE 2.
TO GLYCERIN STRIPPING COLUMN, PAGE 2.
RECYCLE GLYCERIN FROM PAGE 2.
STM.
C.W.
C.W.
VENT
©₂
STM.
C.W.
C.W.
VENT
©₃
LOW PRESS. STEAM
COND.
LOW PRESS. STEAM
COND.
PROCESS WATER
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K₇
PROCESS WATER
WASHED SALT TO DISPOSAL OR IN-PLANT REUSE
K₇
COND. TO COOLING TOWER
K₈
CONDENSATE TO COOLING TOWER
K₆
D
CALENDRIA STYLE DOUBLE EFFECT EVAPORATORS
SALT REMOVAL CENTRIFUGE
CALENDRIA STYLE CONCENTRATOR
SALT REMOVAL CENTRIFUGE
CONCENTRATED RAW GLYCERIN STORAGE TANK (LOW SALT CONTENT)

Fig. II-5. Flow Diagram for a Process Utilizing Vacuum Distillations (Glycerin)

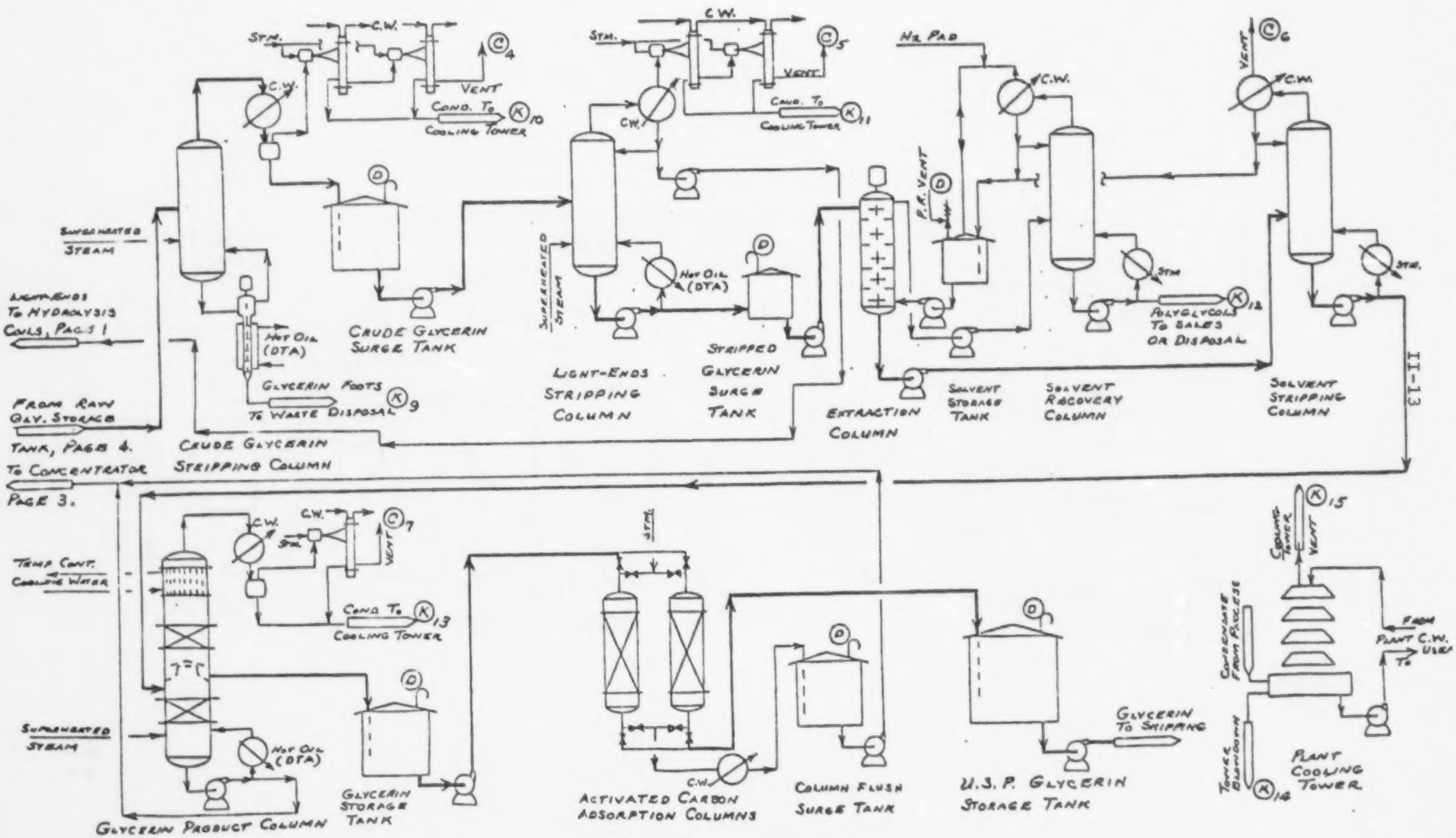

STM.
C.W.
VENT
Cond. To Cooling Tower
C 4
K 10
Superheated Steam
Light-Ends To Hydrolysis Coils, Page 1
Hot Oil (DTA)
Glycerin Foots To Waste Disposal
K 9
From Raw Gly. Storage Tank, Page 4.
To Concentrator Page 3.
Crude Glycerin Stripping Column
D
Crude Glycerin Surge Tank
Superheated Steam
Light-Ends Stripping Column
C 5
K 11
Stripped Glycerin Surge Tank
Extraction Column
P.R. Vent
N2 Pad
Solvent Storage Tank
Solvent Recovery Column
Polyglycols To Sales or Disposal
K 12
C 6
Solvent Stripping Column
II-13
Temp Cont. Cooling Water
Superheated Steam
C 7
K 13
Glycerin Product Column
Glycerin Storage Tank
Activated Carbon Adsorption Columns
Column Flush Surge Tank
U.S.P. Glycerin Storage Tank
Glycerin To Shipping
Cooling Tower Vent
K 15
Condensate From Process
Tower Blowdown
K 14
From Plant C.W. Users
To
Plant Cooling Tower

Fig. II-5. (Continued)

Page 2 of 2

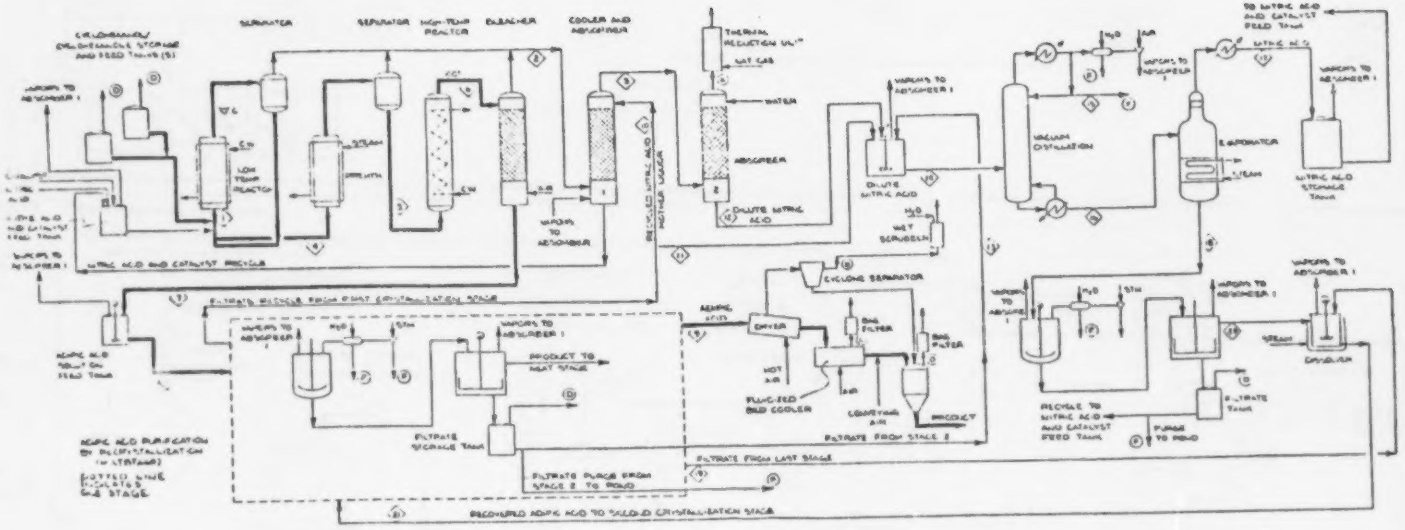

CYCLOHEXANOL/
CYCLOHEXANONE STORAGE
AND FEED TANKS (5)
VAPORS TO
ABSORBER I
SEPARATOR
LOW
TEMP
REACTOR
STEAM
SEPARATOR
HIGH-TEMP
REACTOR
CW
BLEACHER
AIR
COOLER AND
ABSORBER
VAPORS
TO
ABSORBER
NITRIC ACID AND CATALYST RECYCLE
NITRIC ACID
AND CATALYST
FEED TANK
VAPORS TO
ABSORBER I
RECYCLED NITRIC ACID
MOTHER LIQUOR
THERMAL
REDUCTION UNIT
NAT GAS
WATER
ABSORBER
DILUTE NITRIC
ACID
VAPORS TO
ABSORBER I
DILUTE
NITRIC ACID
H_2O
WET
SCRUBBER
CYCLONE SEPARATOR
VACUUM
DISTILLATION
H_2O
AIR
VAPORS TO
ABSORBER I
TO NITRIC ACID
AND CATALYST
FEED TANK
NITRIC ACID
EVAPORATOR
STEAM
VAPORS TO
ABSORBER I
NITRIC ACID
STORAGE
TANK
ADIPIC ACID
SOLUTION
FEED TANK
FILTRATE RECYCLE FROM FIRST CRYSTALLIZATION STAGE
VAPORS TO
ABSORBER I
H_2O
STM
VAPORS TO
ABSORBER I
PRODUCT TO
NEXT STAGE
FILTRATE
STORAGE TANK
ADIPIC ACID PURIFICATION
BY RECRYSTALLIZATION
(4 STAGES)
DOTTED LINE
ISOLATES
ONE STAGE
FILTRATE PURGE FROM
STAGE 2 TO POND
RECOVERED ADIPIC ACID TO SECOND CRYSTALLIZATION STAGE
ADIPIC
ACID
DRYER
HOT
AIR
FLUIDIZED
BED COOLER
AIR
BAG
FILTER
BAG
FILTER
CONVEYING
AIR
PRODUCT
FILTRATE FROM STAGE 2
FILTRATE FROM LAST STAGE
VAPORS
TO
ABSORBER
I
H_2O
STM
VAPORS TO
ABSORBER I
VAPORS TO
ABSORBER I
STEAM
DISSOLVER
FILTRATE
TANK
RECYCLE TO
NITRIC ACID
AND CATALYST
FEED TANK
PURGE
TO POND

Fig. II-6. Flow Diagram for a Process Utilizing Vacuum Crystallizers (Adipic Acid)

and 31% of the distillation systems in the data base of products surveyed[19] utilize vacuum. It must be emphasized that these plant designs do not necessarily represent existing plants and that the selection of products in that data base may be biased toward large-capacity products.

It appears that nearly one-third of all distillation systems operate under vacuum and that perhaps one-tenth of the other unit operations except for filtration operate under vacuum. No data on vacuum filtration are available, but it is estimated that at least one-tenth and possibly much more of the continuous filtration operations in SOCMI utilize vacuum filtration equipment.

IT Enviroscience has estimated that about 3600 distillation units are used by SOCMI. This estimate is based on actual counts of distillation equipment at each site from data submitted early in this study and an estimate of the total number of sites in SOCMI. If one-third are vacuum units, then about 1200 vacuum distillation units exist. At an emission rate of 15 lb/hr (estimated from the IT Enviroscience data on vacuum distillations), vacuum-distillation operations alone could represent 158 million lb of VOC emissions per year at the present level of control. Another EPA contractor is collecting more data on distillation emissions and will be able to improve the organic emission estimate.

III. DESCRIPTION OF EMISSION

A. FLOW RATE

The flow from a vacuum device is determined by the noncondensed vapors and gases that pass through the contact or surface condensers or liquid seals (if any) in the vacuum device. These carrier gases enter the system through leaks, through blankets, as dissolved gases in liquid or solid feeds, and/or as gases or vapor generated in the equipment or in the vacuum-device condensers or seals. Inorganic carrier gases are discussed here; the organic carrier gases and other VOC are discussed in Section B.

1. Leaks

An operation under vacuum will have a tendency to leak. Any seal imperfections, or other discontinuities will allow air to enter the system under vacuum. A designer of the vacuum system must include the noncondensable gas load from the leaks into the vacuum device design before the process unit is constructed. Until recently there were two approaches to this estimate. The first approach may be used when a detailed design of the vacuum equipment is known; then each flange, fitting, and seal may be categorized and the total leak rate of the equipment estimated from published factors.[20] Table III-1 lists these leak factors.

The second approach for leak rate estimation depends on the approximate size of the vacuum vessel.[20] With a vacuum distillation unit used as an example, the diameter of the distillation equipment depends mostly on the vapor flow up through the column, which in turn is dependent on the vapor density, feed rate, and reflux ratio. The height depends on the vapor-liquid equilibrium data and the compositions of the feed, distillate, and bottoms (highly specific to the application). The volume of the vessel cannot easily be predicted simply through knowledge of the plant capacity and product. The same is true for reactors and other unit operations. The approach requires quite detailed knowledge of the volumes and sizes of each vacuum process unit.

Table III-1. Leak Rates of Fittings in Vacuum Equipment[a]

Fittings	Estimated Average Leak Rate (lb/hr)	(scfm)[b]
Screwed connections to 2 in.	0.1	0.02
Screwed connections above 2 in.	0.2	0.04
Flanged connections to 6 in.	0.5	0.10
Flanged connections from 6 to 24 in., including manholes	0.8	0.17
Flanged connections 24 in. to 6 ft	1.1	0.23
Flanged connections above 6 ft	2.0	0.41
Packed valves to 1/2 in. in stem diameter	0.5	0.10
Packed valves above 1/2 in. in stem diameter	1.0	0.21
Lubricated plug valves	0.1	0.02
Petcocks	0.2	0.04
Sight glasses	1.0	0.21
Gage glasses including gage cocks	2.0	0.41
Liquid-sealed stuffing box for shafts (per in. of shaft diameter)	0.3	0.06
Ordinary stuffing box (per in. of shaft diameter)	1.5	0.31
Safety valves and vacuum breakers (per in. of nominal size)	1.0	0.21

[a] From ref 20.

[b] As air with a molecular weight of 29.

Figure III-1 (bottom chart) shows the relationship of system volume to diameters and heights. Zones for typical dimensions of process equipment are shown. If realistic dimensions of distillation systems and reactors or crystallizers can be estimated, the system volume can be approximated and Fig. III-1 (top chart) can be used to approximate the leak rate. This rate should be multiplied by 0.5 to 0.75 for a tightly run plant with minimum leaks or by a factor of 2 to 3 for a plant without good leak control.[9,21]

With enough maintenance and effort, any vacuum vessel may be made essentially leak free. However, there is an optimum effort at which the cost of leak

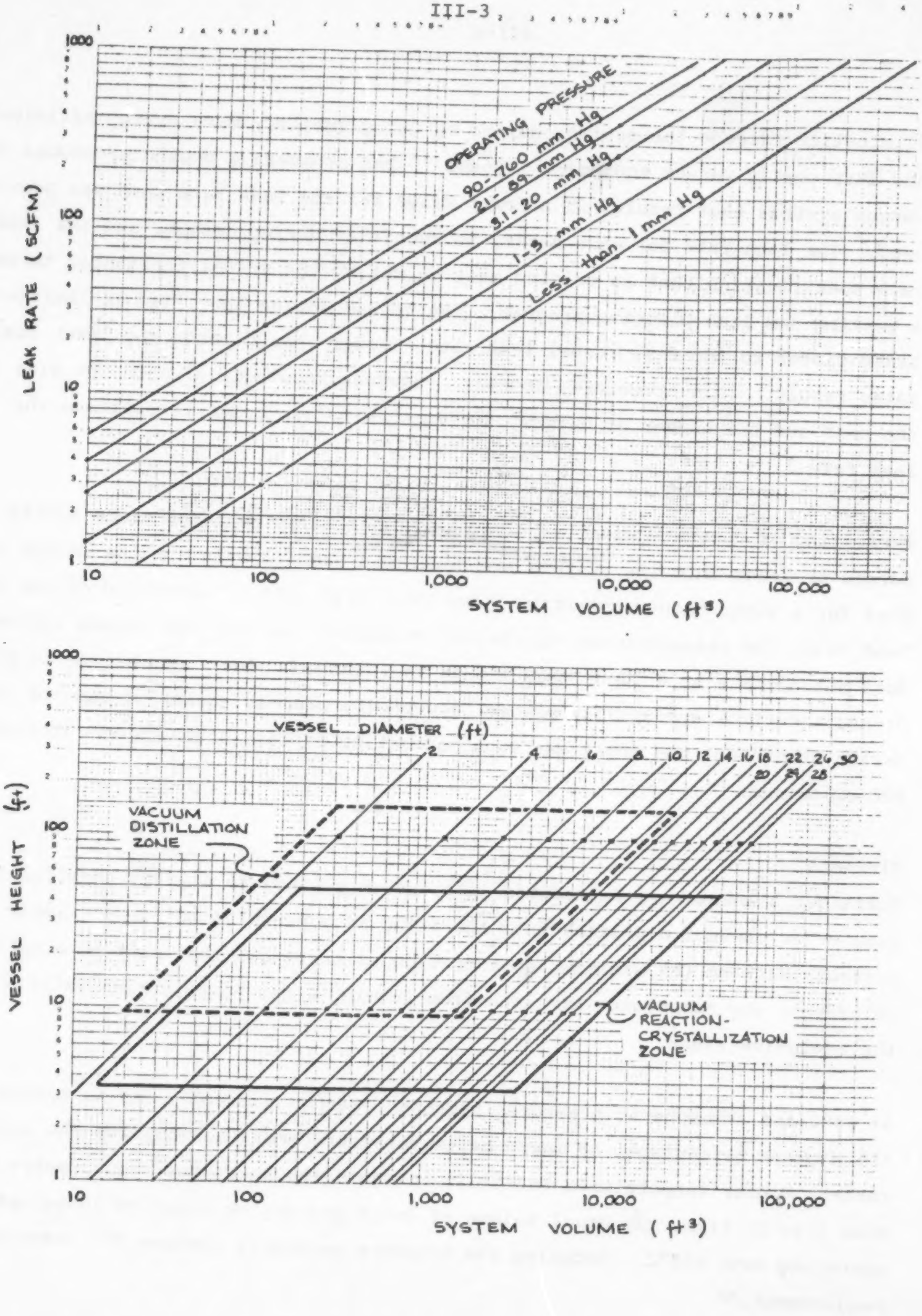


Fig. III-1. Estimation of a Vacuum System's Leak Rate from Equipment Dimensions

elimination exceeds the savings gained by using smaller, more energy-efficient, and less costly vacuum equipment. Ryans [17] has proposed a design procedure for vacuum systems that results in a lower value for the leak rate than was previously used. The leak rate for each vessel is specified during design, and the leak rate specification that is written must be met by the vessel fabricator through a testing and leak plugging program. The vacuum source specified is therefore sized closer to the real vessel leak rate. Lower energy costs and lower leak rates result. This procedure, however, requires knowledge of both the size of the unit and the number of valves, fittings, etc., in order to estimate the leak rate.[17]

Oversizing of vacuum devices may lead to higher emission rates since artificial purges or leaks into the systems are sometimes used to maintain the design vacuum. Thus for a given vacuum operation whose real leak rate is one-third of the design leak rate, the remaining two-thirds may be bled-in so that the vacuum system does not operate at a lower vacuum than is required. Inert gas bleeds to provide pressure control are usually placed between the process equipment and the vacuum device to prevent the inert gas from contacting process organics and increasing VOC emissions.

2. Blankets

Inert-gas blankets are introduced into vacuum systems to prevent chemical decomposition or to prevent a process from operating in the explosion range. Table III-2 presents data on the minimum concentration of inert gas that must be established to prevent any subsequent air leak from forming a gas mixture that falls within the explosive range.

At 25°C and atmospheric pressure, hydrogen, carbon monoxide, and acetylene require the highest percentages of inert gases to ensure operation outside the explosive range. Higher temperatures radically increase the inert-gas requirements so that 5 to 10 times the usual volume of inert gas may be required in equipment operating near 100°C. Reducing the pressure generally reduces the inert-gas requirement.[22]

The factors in Table III-3 can be used to estimate the contribution of inert gases to the total gas flow. These factors may be used with the air leak rate

Table III-2. Minimum Inert-Gas Concentration for Operation to Be Entirely Out of the Explosion Envelope[a]

Compound	Inert-Gas Concentration[b] (mole %)	
	CO_2	N_2
Methane	23	37
Ethane	31	44
Propane	28	43
Butane	28	40
N-Pentane	29	42
N-Hexane	29	42
Higher paraffins	28	42
Ethylene	39	49
Propylene	28	42
Isobutylene	26	40
1-Butene	31	44
3-Methyl-1-butene	31	44
Butadiene	35	48
Acetylene	53	65
Benzene	29	43
Cyclopropane	30	41
Methanol	32	46
Ethanol	33	45
Dimethyl ether	33	48
Diethyl ether	34	49
Methyl formate	33	45
Isobutyl formate	26	40
Methyl acetate	29	44
Acetone	28	43
Methyl ethyl ketone	34	45
Hydrogen sulfide	30	
Hydrogen	56	72
Carbon monoxide	41	58

[a] See ref 22.

[b] Does not include the inert gas related to the air concentration. Values expressed are for mixture at 25°C and 760 mm Hg. Operation under vacuum will not require as high inert concentration as those expressed.

to estimate emission rates from vacuum operation when inert-gas blankets are used to prevent operation in the explosion range.

Table III-3. Inert-Gas-Flow Estimates to Prevent Operation in the Explosion Range[a]

	Volume of Inert Gas Required for Each Volume of Air[b]	
	At 25°C	At 100 to 150°C
Organic gases and vapors	0.25—1	3—10
Flammable inorganic gases and acetylene	0.8—3	5—10

[a] From ref. 22; for use in estimating vacuum system emission rates only; not used for equipment design.

[b] Can be used with leak rate prediction procedure.

The use of blanketing to prevent chemical decomposition usually implies that the decomposition is related to the presence of oxygen in the process. Although the oxygen restriction required to prevent decomposition may differ from that required to prevent explosion, the inert-gas ratios shown in Table III-3 can be considered as minimum levels of inert gas required for either purpose.

3. Dissolved Gases

Liquids and solids introduced into a vacuum process may carry noncondensable gases with them. Under vacuum these gases will be released and will contribute to the vacuum-device emission. A brief summary of a few gases dissolved in some compounds is presented in Table III-4.[23] Although not comprehensive, these data show the magnitude of the flow of gases originating from gases dissolved in liquids. For those cases where the pressures of the feeds are near-atmospheric the contribution of carrier gases from this source ranges from 0.1 to 10 scfm/100 million lb of feed per year to the vacuum system. Except when the systems have a very large capacity or when the liquids come directly from high-pressure operation, this source is insignificant.

Table III-4. Contribution of Carrier Gases from Dissolved Gases in Organic Liquids[a]

	Gas Flow[b] (scfm/100 MM lb of liquid/yr)			
Organic Liquid	H_2	N_2	CH_4	CO_2
n-Perfluoroheptane	0.25	0.68	1.45	3.68
n-Heptane	0.47			8.26
Carbon tetrachloride	0.14	0.28	1.26	4.75
Carbon disulfide	0.13	0.20	1.18	2.95
Acetone	0.27	0.70	2.63	

[a] Adapted from ref 23.

[b] At 25°C and atmospheric pressure.

Vacuum devices sometimes utilize contact condensers or water seals. The water introduced to the vacuum also can contain dissolved carrier gases. Table III-5 gives the range of gas flow from this source.

Table III-5. Carrier Gas Flow from Contact Condensers or Seal Water*

	Gas Flow for 1000-gpm Water	
Water Temperature (°F)	(lb/hr)	(scfm)
40	16.8	3.47
50	14.9	3.07
60	13.2	2.72
70	11.8	2.43
80	10.7	2.21
90	9.7	2.00
100	8.8	1.82

*From ref 11.

Water consumption may be estimated from the steam consumption rate for a steam ejector. The steam consumption (in lb/hr) times 0.06 is the approximate water consumption in gpm.

The ranges of steam consumption and therefore the water consumption and dissolved gas flow for various types of ejector systems are given in Table III-6. Except for five- or six-stage systems operating at low pressures, carrier gases absorbed in the cooling water are less than 10% of those that leak in the system.[9—11]

Table III-6. Steam Consumption, Water Consumption, and Steam-Ejector Gas Flow from Water-Dissolved Gases[a]

Type of System	Steam Consumption (lb of steam/lb of air)	Water Consumption (gal of H_2O/lb of air)	Gas Flow[b] (scf of gas/scf of air)
Single stage	1.5—30	5—108	0.001—0.022
Two stage	7—40	25—144	0.005—0.030
Three stage	1—40	4—144	0.001—0.030
Four stage	20—100	72—360	0.015—0.074
Five stage	50—175	180—630	0.037—0.130
Six stage	200—1000	720—3600	0.149—0.743

[a] From refs 9 and 11.

[b] Water temperature, 70°F.

4. Chemical Decomposition

Some compounds undergo reactions that result in the formation of potential carrier gases in chemical equipment and, as was noted earlier, is one of the reasons why process equipment is operated under vacuum. Lower pressures usually mean lower temperatures and less chemical decomposition. Gases formed by chemical decomposition are highly specific and difficult to predict without specific data about the process concerned. If, for instance, carbon is being oxidized to CO or CO_2, then at least 1 mole of gas will be generated for each carbon atom in the feed molecule. In other words, oxidation of a ten-carbon molecule could form 10 moles of gas and probably 10 moles of water vapor for each mole of feed oxidized. In a vacuum process the water vapor is condensed and does not increase the flow rate of the final emission.

The decomposition rate is probably not a function of throughput. In, say, oxidation the oxygen required to oxidize the organic molecules may be available only at the liquid-gas interface. This surface area may be constant and independent of feed rate for any single piece of equipment but may increase as equipment size increases. Therefore decomposition rates cannot be estimated on the basis of product and plant capacity. Further complicating the problem, potential carrier gases generated during decomposition may undergo further reactions, which result in no net change in total gas volume.

The following simple case will be assumed to estimate the order-of-magnitude range for gases generated by chemical decomposition. A chemical with a molecular weight of 100 is being processed in vacuum equipment at the rate of 1 to 1000 lb/hr; 10 mole % of this material is decomposed to a gas. The number of moles of gas produced is equal to the number of moles of chemical decomposed. The data from the calculation are presented in Table III-7.

Table III-7. Carrier Gas Flow from Chemical Decomposition
(equimolar gas evolving from 10 mole % of the feed decomposed)

Feed Rate		Decomposition Carrier Gas Rate	
(lb-moles/hr)	(lb/hr)*	(lb-mole/hr)	(scfm)
0.01	1	0.001	0.006
0.1	10	0.01	0.06
1.0	100	0.1	0.6
10.0	1000	1.0	6.0
100.0	10,000	10.0	60.0

*Based on a molecular weight of 100.

B. VOC CONCENTRATION

The maximum concentration of VOC for a single organic component under ideal conditions can be given by a combination of Dalton's and Raoult's laws:

$$y = \frac{xp}{\pi} , \qquad (1)$$

where y is the mole fraction of the component in the vapor, x is the mole fraction of the component in the liquid, p is the vapor pressure of the component at the system temperature, and π is the total pressure of the system. In this expression thermodynamic equilibrium or saturation of the component in the vapor is assumed. Depending on a variety of considerations the gases leaving a vacuum device may or may not be saturated. This analysis will not apply exactly to multicomponent organic systems, but analogous effects will be assumed.

Figure III-2 shows a vacuum operation with steam ejectors and surface condensers. The cooling water to the condenser does not contact the condensed steam nor the carrier gases. Liquids that form are separated from the carrier gases in the condenser. Organics that condense with the steam condensate will either separate as a second phase from the condensed liquid or remain soluble in the water. If a second phase is formed with a single component, Eq.(1) should apply. The mole fraction in the liquid (second phase) would equal 1 and the vapors should be saturated at condenser outlet conditions. If there is only an aqueous phase, then x would be less than 1 and y should be considerably less than saturation.

A vacuum operation with steam ejectors and contact condensers is shown in Fig. III-3. This system differs from a steam ejector with a surface condenser in that water is added directly to the steam discharge from the ejector. The water intimately contacts and cools the vapors, which are condensed. Organics can generate two phases in this type of unit, but, since the added water considerably dilutes the mixture, a single aqueous phase is much more likely. Typically, then, the organic concentration in the gas stream from the separation chamber (hot well) may be less than that in a steam ejector with a surface condenser. However, organics leaving in the aqueous liquid must be treated and could be a source of secondary emissions. Surface condensers have the advantage over contact condensers of potential recovery of the organic from a smaller volume of liquid discharge.

Figure III-4 shows a vacuum process with water-sealed vacuum pumps. Water-sealed vacuum pumps use water or other liquids for the sealant, which is flushed once through the device or is recirculated through a small seal tank. In the case of a seal tank a certain amount is then discharged on either a batch or a continuous basis. Since no steam is used in vacuum pumps, the cooling requirements are lower and the ratio of the water fed to the organics condensed can be

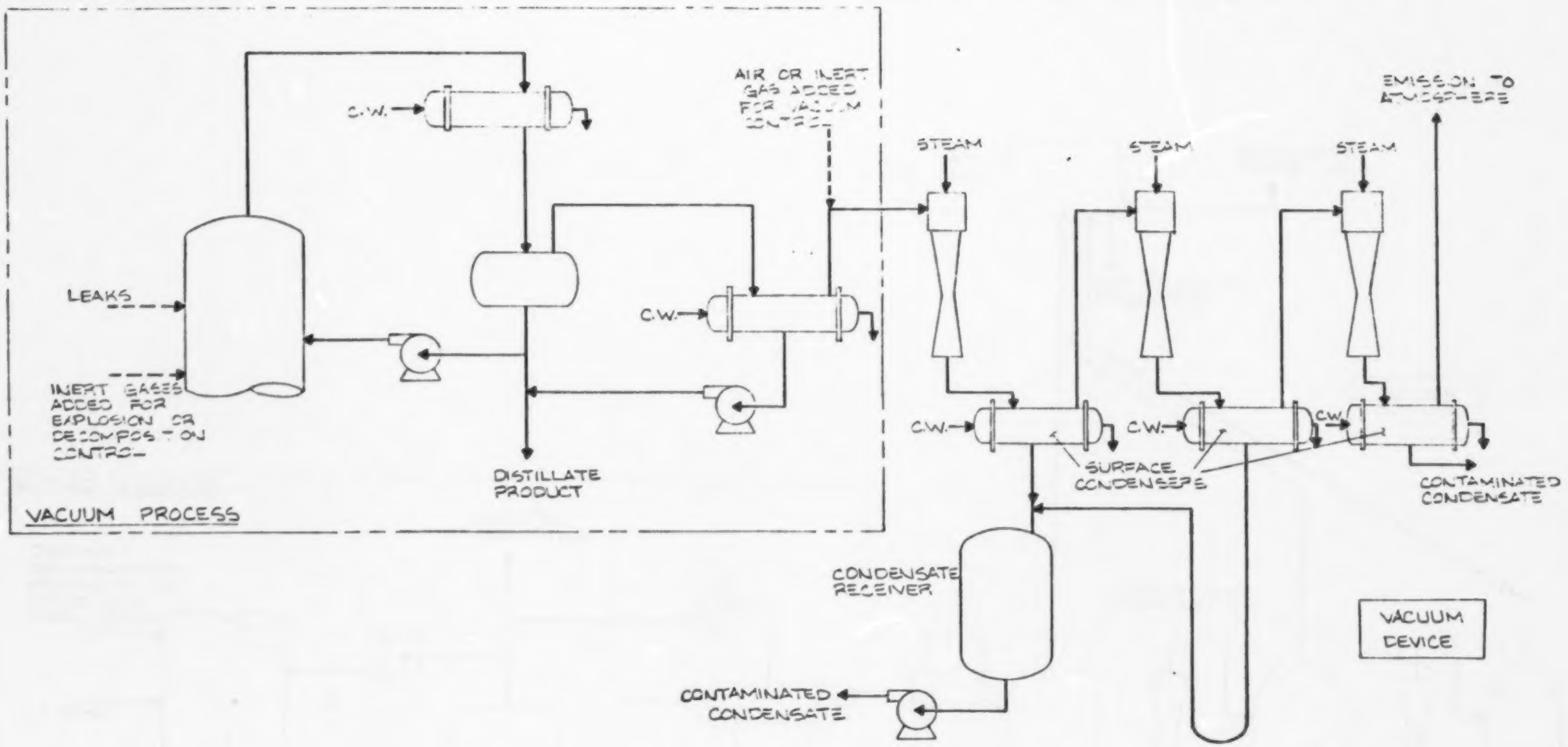
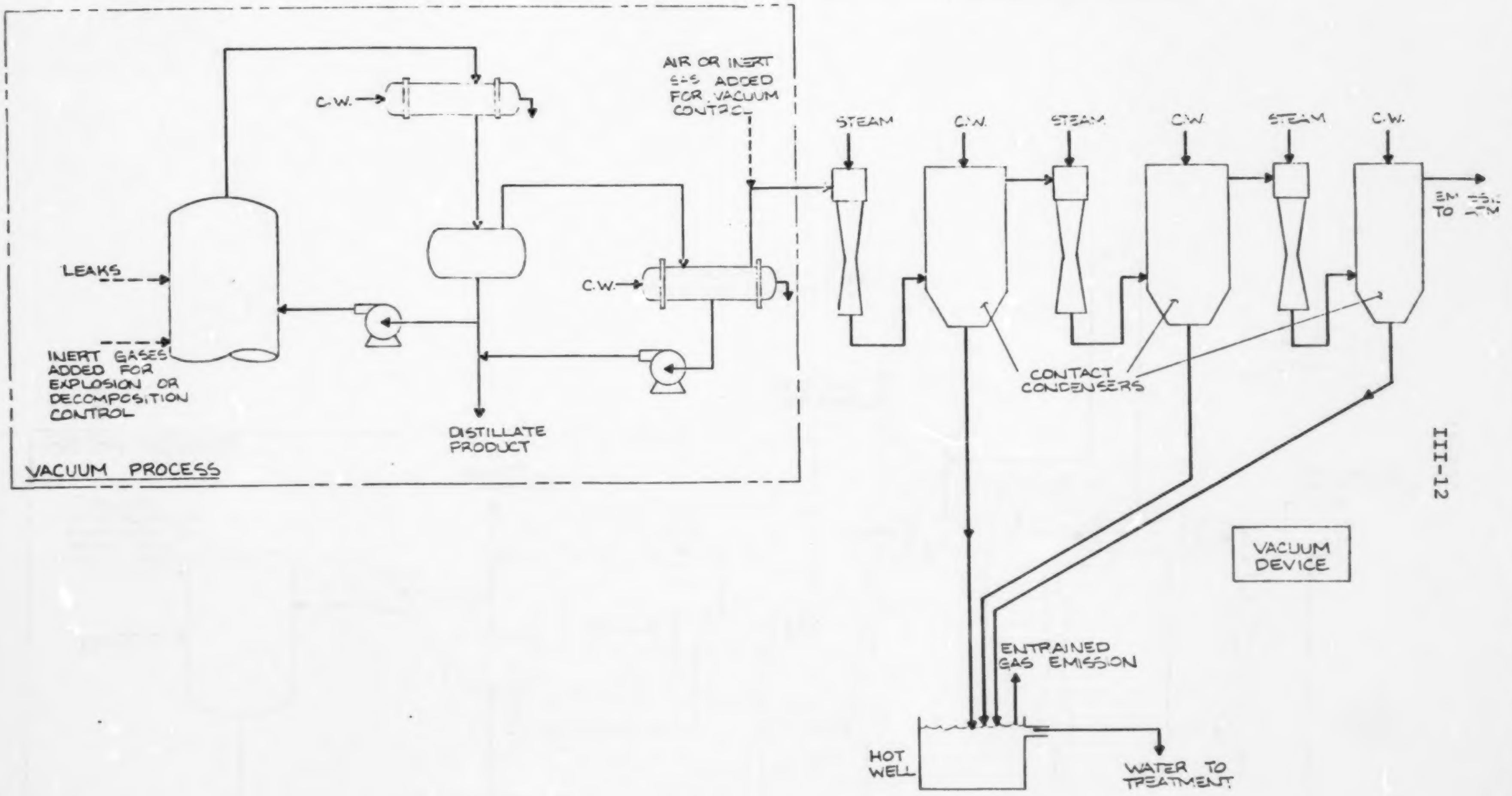

VACUUM PROCESS
LEAKS
INERT GASES ADDED FOR EXPLOSION OR DECOMPOSITION CONTROL
C.W.
C.W.
DISTILLATE PRODUCT
AIR OR INERT GAS ADDED FOR VACUUM CONTROL
STEAM
STEAM
STEAM
EMISSION TO ATMOSPHERE
C.W.
C.W.
C.W.
SURFACE CONDENSERS
CONTAMINATED CONDENSATE
CONDENSATE RECEIVER
CONTAMINATED CONDENSATE
VACUUM DEVICE

Fig. III-2. Vacuum Process with Surface Condensers and Condensate Receiver



AIR OR INERT GAS ADDED FOR VACUUM CONTROL
C.W.
LEAKS
INERT GASES ADDED FOR EXPLOSION OR DECOMPOSITION CONTROL
C.W.
DISTILLATE PRODUCT
VACUUM PROCESS
STEAM
C.W.
STEAM
C.W.
STEAM
C.W.
EMISSION TO ATM
CONTACT CONDENSERS
VACUUM DEVICE
ENTRAINED GAS EMISSION
HOT WELL
WATER TO TREATMENT

Fig. III-3. Vacuum Process with Contact Condensers and Barometric Seal

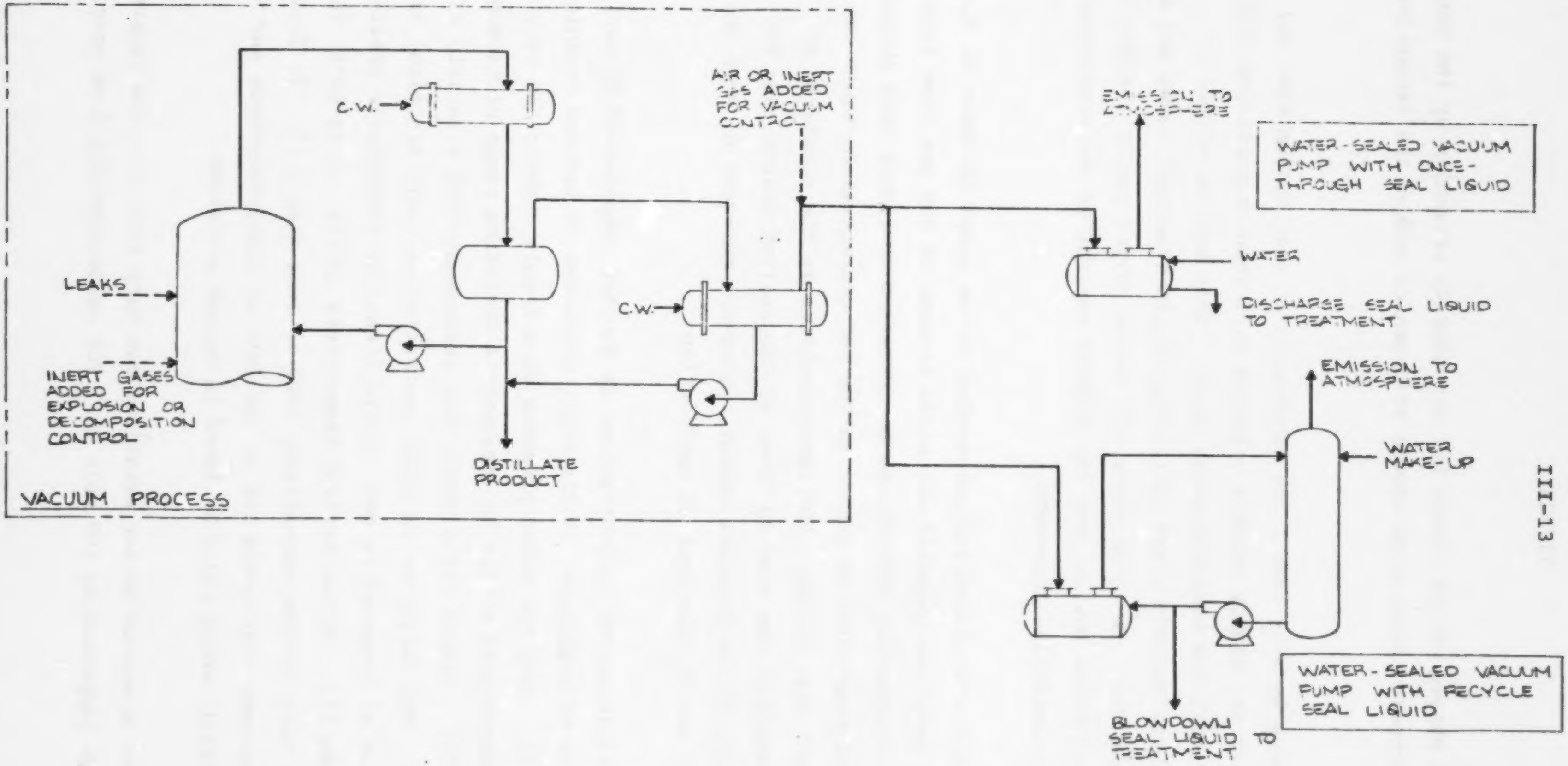

C.W.
AIR OR INERT GAS ADDED FOR VACUUM CONTROL
EMISSION TO ATMOSPHERE
WATER-SEALED VACUUM PUMP WITH ONCE-THROUGH SEAL LIQUID
WATER
DISCHARGE SEAL LIQUID TO TREATMENT
LEAKS
C.W.
INERT GASES ADDED FOR EXPLOSION OR DECOMPOSITION CONTROL
EMISSION TO ATMOSPHERE
WATER MAKE-UP
DISTILLATE PRODUCT
VACUUM PROCESS
WATER-SEALED VACUUM PUMP WITH RECYCLE SEAL LIQUID
BLOWDOWN SEAL LIQUID TO TREATMENT

Fig. III-4. Vacuum Process with Water-Sealed Vacuum Pumps

very low. Organic phases can be formed but are usually prevented by the water flow rate being increased since high levels of organics reduce the vacuum potential of the device.

For all cases where x is less than 1 the condensing or seal system also may act as an absorber; that is, highly soluble organics will tend to partition with the liquid and not with the noncondensable gases. This has the effect of lowering potential air emissions and increasing liquid treatment needs and potential secondary emissions. In these cases the vacuum device can be thought of as an air emission control device; but the organic content of the wastewater or the water pollution potential increases.

A vacuum process with oil-sealed and gas-sealed vacuum pumps is shown in Fig. III-5. Oil-sealed vacuum pumps can generate oil mists because of the gas flow through the system. Mist-eliminating devices can be installed to reduce this emission impact. Gas-sealed pumps have no impact on the VOC concentration since the gases do not contact seal fluids. VOC concentrations in the discharge of gas-sealed pumps would be the same as those at the suction unless some VOC is condensed by virture of the pressure change. However, gas-sealed pumps are not often selected for use in this type of application.

The problem of estimating VOC concentrations is further complicated by variation, over several orders of magnitude, of the vapor pressures of various organics [crucial to Eq.(1)]. Even the vapor pressure of a single organic can vary widely over differing temperatures within the reasonable operating range of vacuum devices (10 to 60°C). Figure III-6 shows this phenomenon with a variety of organic compounds. The variation in vapor concentration (mole fraction) is given as a function of temperature over a pure liquid at atmospheric pressure as calculated by Eq.(1). Within certain temperature limits, 10 to 60°C, the mole fraction can vary between essentially 100% to less than 0.1%. In fact, there are may compounds that would lie to the left of dichloromethane and to the right of o-cresol, which could be found in vacuum processes.

VOC concentrations in vacuum device emissions can vary from very low (approaching zero) to very high (approaching 100 mole %). VOC concentrations from specific

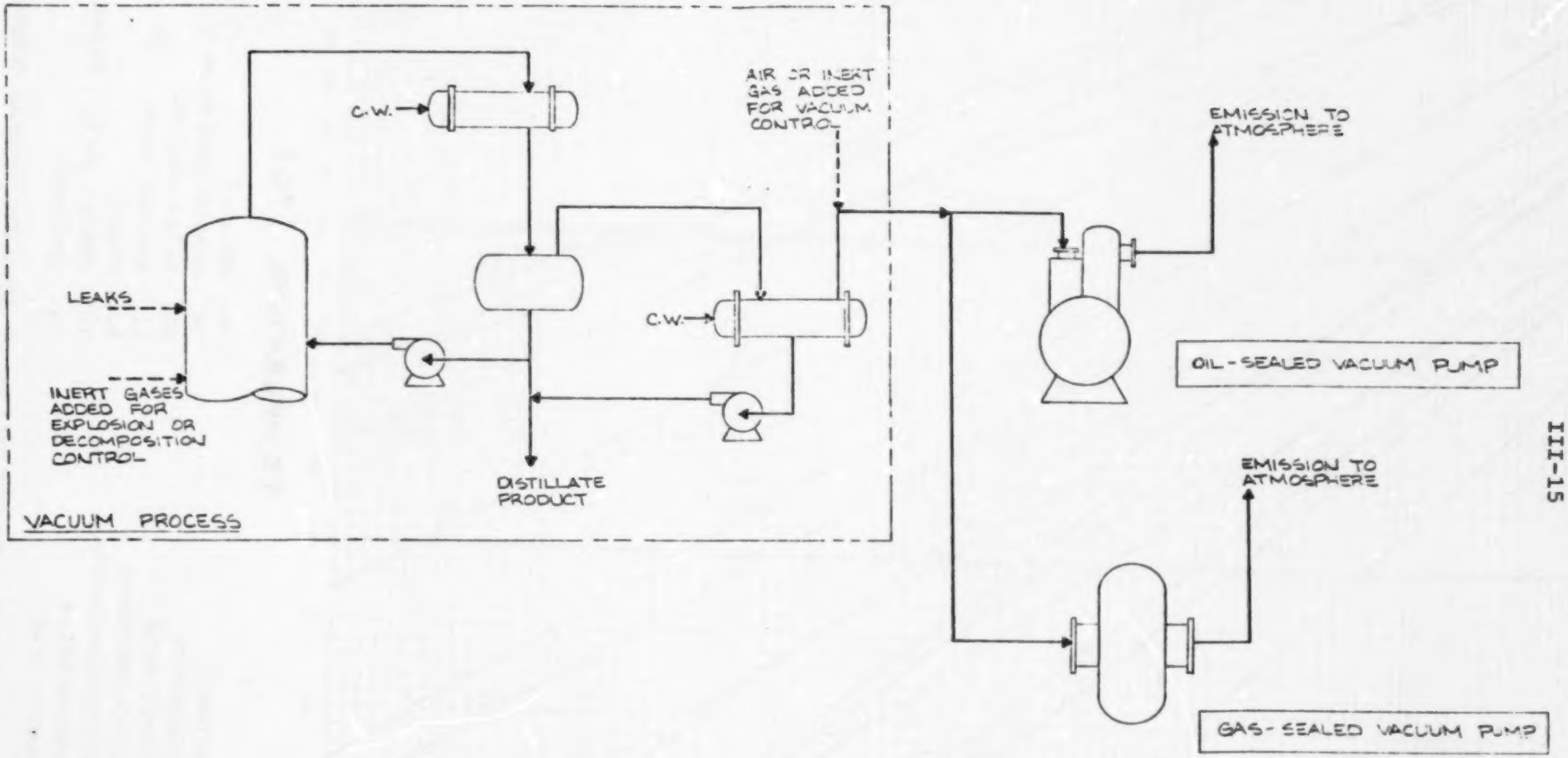
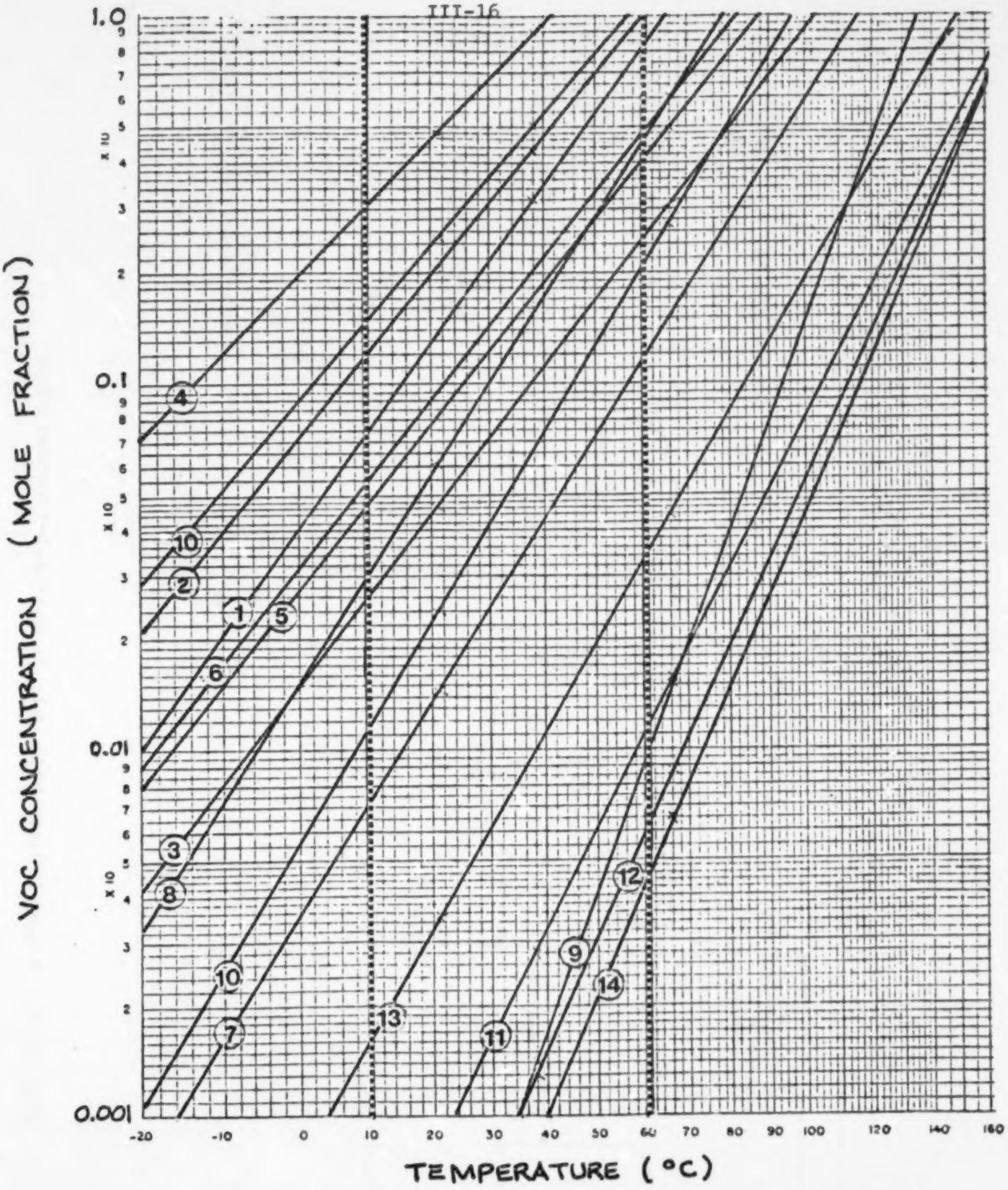

C.W.
AIR OR INERT GAS ADDED FOR VACUUM CONTROL
EMISSION TO ATMOSPHERE
LEAKS
C.W.
OIL-SEALED VACUUM PUMP
INERT GASES ADDED FOR EXPLOSION OR DECOMPOSITION CONTROL
DISTILLATE PRODUCT
EMISSION TO ATMOSPHERE
VACUUM PROCESS
GAS-SEALED VACUUM PUMP

Fig.III-5. Vacuum Process with Oil- or Gas-Sealed Vacuum Pumps



1. Methanol
2. Chloroform
3. Formic acid
4. Dichloromethane
5. Trichloroethylene
6. Acetonitrile
7. Acetic acid
8. Ethanol
9. Monoethanolamine
10. Allyl alcohol
11. Butyric acid
12. Phenol
13. Methyl phenyl ether
14. o-Cresol

Fig. III-6. Saturation Concentrations of Specific Organic Compounds in Gas

sources can be defined only if components, temperatures, vapor pressure, and other physical property data are known for that specific emission.

C. ACTUAL VACUUM SYSTEM EMISSIONS

Actual data for VOC emissions from vacuum systems are given in Table III-8; the data were obtained from the sources cited in the Appendix. Both uncontrolled and controlled data are given and the control device is noted. The emission flow rates range from less than 1 scfm to 1300 scfm, whereas concentrations range from nearly zero to nearly 100 mole %, and shows relatively good agreement with the flow and concentrations developed in this report. It is not possible to verify the relationship between flow and equipment size since information on the latter was not collected during the IT Enviroscience study.

Table III-8. Actual Emission Data from Vacuum Systems

	Uncontrolled			Controlled				VOC Emissions (lb/hr)		
Type of Equipment	Flow (scfm)	VOC Concentration (mole %)	Temperature (°C)	Flow (scfm)	VOC Concentration (mole %)	Temperature (°C)	Control Device	Uncontrolled	Controlled	Emitted to Atmosphere
Crystallizer	330		49							
	1252	0.11	38				Condenser	11.4		11.4
Evaporator				3.3	0.7	35	Condenser		0.29	0.29
				0.01	100	38	Condenser		0.08	0.08
Distillation	8.47	8.0	30				Caustic Scrubber	11.2	0.11	0.11
				1.67	22.9		Condenser		4.1	4.1
		0.6					a			0.6
							Condenser		2.45	2.45
	1408[b]	0.36	99	148	10.9		Condenser then flare	76.1	18.9	18.9 (to flare)
(3 units)	85	32	41	55	1.3		Condenser	401	6.2	6.2
(6 units)	255	52.2	49	130	20.2	1	Condenser	1460	325	325
					~100		Condenser		14	14
	80						a			
	2.95[b]	~100	100					13.4		13.4
	216	0.45	30					13.7		13.7
	100						a			
			100			60	Scrubber	16.7		
			100			60	Scrubber	2.1	8.3	8.3
			100			60	Scrubber	4.2		
			100			60	Scrubber	0.21		
			60					0.42		0.42
	42.7	0.2						2		
	42.9	0.7	35	44.5	1.62	45	Manifold-condenser	6	14	14
	42.9	0.7	35					6		
	355[b]	0.66	96					30.6	c	30.6
	3.55	0.92	35-40	3.5	0.34	35	Condenser	0.44	0.17	0.17
	54.8	4.2	35-40	52.7	200 ppm	35-40	Condenser	29.9	0.13	0.13
	73.4	4.5	35-40	70.1	40 ppm		Condenser	44.2	0.1	0.1
	3.1	31.2	30-40	2.31	7.5	20-30	Condenser	13.0	2.3	2.3

[a] Level of control is unknown.

[b] High temperature reported indicate flow may contain ejector stream.

[c] Controls planned.

IV. CONTROL OPTIONS FOR VACUUM SYSTEMS

A. IN-PROCESS CONTROL

Both in-process and add-on control techniques or devices have been used for vacuum systems. Carrier-gas flow can be reduced by not oversizing the vacuum device by as large a factor as is presently used. This design is more energy efficent, and the lower flows that result may also result in lower organic emissions. Emissions from processes in which gases are bled into the system for preventing decomposition or explosion or for control of the vacuum may be partly controlled through the recycle of exhaust gases from the vacuum source to the bleed line. This approach cannot entirely eliminate the emission since the leak rate will continue regardless of the recycle. Therefore the flow of the vacuum source emission can be reduced to the level of the leak rate but no further. This, however, can result in a significant emission reduction.

Design of vacuum systems incorporating surface condensers may provide for the recovery of organic chemicals and the reduction of total water and air pollution. However, in some cases the systems may tend to increase the concentration of the air emissions since the noncondensed gases may come into contact with essentially pure organic compounds. In this case water pollution (treatment loads or potential secondary emissions) may diminish at the expense of increasing air losses.

B. ADD-ON CONTROLS

Control devices added to ejector-type vacuum devices must be capable of handling relatively large variations in flow rate at low pressure drops. The flow rate from ejectors changes quickly if the suction pressure changes. Increased leaks due to equipment aging or thermal cycling can increase the flows significantly. A control device that generates significant back-pressure can reduce the capacity of vacuum sources. In new plants this may be accounted for by appropriate sizing of the vacuum device. In existing plants, however, this effect may require a booster device to overcome the increased discharge pressure drop related to the control.

Vacuum devices utilizing water seals or contact condensers will produce emissions saturated with water at the temperature of the exhaust. This water vapor can significantly affect the design of add-on control devices. For instance, carbon adsorption loadings may be lowered if the emission is not dehumidified prior to control. Water vapor may limit the temperature at which an aftercondenser may be operated since ice could form and plug the condenser.

A variety of control devices for organic emissions have been reported in various control device evaluation reports. These reports describe the limitations of each control device and offer costs as functions of the applicable flow and composition ranges for each device. Table IV-1 summarizes the cost effectiveness for each control technology for a typical case. This table should be used only to identify the most cost-effective technologies in a general way since other considerations may cause the costs to change. When a control technology is selected, the control device evaluation reports may be used to more completely identify the costs.

Vacuum systems can generate waste gases with flows of from less than 1 scfm to 10,000 scfm and with VOC concentrations of from nearly zero to nearly 100 mole %. All control devices could therefore be applied, depending on the specifics for each stream.

Condensation is most appropriate for waste gases with flows of under 5000 scfm. It is effective only when the VOC present is condensible, or in other words not an organic carrier gas. After-condensers and refrigerated condensers are widely used to control vacuum system emissions. Further information on condensation is available in the control device evaluation report on condensation.

Absorption is also used for control of vacuum systems emissions and is also discussed in more detail in a control device evaluation report.

Carbon adsorption can be applied only at low-VOC concentrations. It compares attractively to all control technologies on a cost-effectiveness basis. However, in addition to its concentration limitations, carbon adsorption is not effective on a number of organic compounds. When applicable, carbon adsorption is expected to be highly cost-effective. A control device evaluation report on adsorption more completely defines its limitations.

Table IV-1. Representative Cost-Effectiveness for Organic Emission Control Technology

Waste Gas Flow (scfm)	VOC Concentration[a]	Cost Effectiveness (per lb of VOC) for Condensation[b]	Absorption[c]	Adsorption[d]	Flares[e]	Catalytic Oxidation[f]	Thermal Oxidation[g]	High-Temperature Oxidation[h]
500—700	Low	$0.20	i	i	j	$0.31—0.37	$0.55—0.62	$0.78—1.29
	Medium	0.03	i	i	j	k	0.09—0.11	0.20—0.30
	High	0.06	i	i	i	k	0.06	0.12—0.17
1000	Low	0.14	$0.56—1.07	$0.13—0.15	j	i	i	i
	Medium	0.02	0.06—0.11	k	j	k	i	i
	High	0.04	i	k	$0.001	k	i	i
5,000	Low	l	0.20—0.55	0.06—0.08	j	0.09—0.12	0.25—0.29	0.44—0.78
	Medium	l	0.04—0.08	k	j	k	0.02—0.04	0.13—0.19
	High	l	i	k	i	k	0.01	0.09—0.12
50,000	Low	l	0.02—0.18	0.03—0.05	j	0.05—0.07	0.20—0.24	0.37
	Medium	l	0.10—0.45	k	j	k	0.01—0.02	0.11
	High	l	i	k	i	k	0.007	0.08

[a] Low ≅ 0.5 vol % or 10 Btu/scf; medium ≅ 5 vol % or 50 Btu/scf; high ≅ 20 vol % or 100 Btu/scf.

[b] 95% removal efficiency; no VOC credit.

[c] 99% removal efficiency; $L_m/mG_m = 1.4$; steam ratio = 0.2 moles of steam/mole of waste gas; no VOC credit.

[d] 70—12 ppm effluent; 6.96 lb of carbon/1000 scf; no VOC credit; loading - 0.1 lb of VOC/lb of carbon, molecular weight of VOC = 50.

[e] Based on 100% VOC of propylene at 100% of capacity. Flares normally operate intermittently at a low fraction of capacity.

[f] 90—90% destruction efficiency; no heat recovery.

[g] 90—99% destruction efficiency; no heat recovery, 1400—1600°F combustion temperature..

[h] 99.9% destruction efficiency; no heat recovery, 2200—2600°F combustion temperature.

[i] Costs not available.

[j] Not applicable at low concentrations.

[k] Not applicable at high concentrations.

[l] Not applicable at high flow rates.

Catalytic oxidation is applicable only for low-VOC-concentration waste gases as long as catalyst poisons aren't present. Catalytic oxidation can be more cost effective than thermal oxidation if it can be applied to the waste gas. Further information may be found in the control device evaluation report on catalytic oxidation.

Thermal oxidation applies to the flow range and concentration range of waste gases from vacuum systems. In addition, all organic compounds can be oxidized in thermal oxidation units. This type of control is discussed in the thermal oxidation control device evaluation.

When compounds containing sulfur or other particular elements are present in the waste gas, noxious compounds are emitted in the flue gas. Scrubbers are then required to remove the noxious gases from the flue gas prior to discharge. When chlorine-containing compounds are present, the combustion temperature must be increased to convert the Cl to HCl instead of to Cl_2. This aids the removal of chlorine from the flue gas. These special cases of thermal oxidation are discussed in the thermal oxidation supplementary control device evaluation.

V. SUMMARY

Vacuum operations are widespread in SOCMI and account for significant levels of VOC emissions. The emissions from vacuum devices can be characterized according to their flow and VOC concentration.

The total emission flow from a vacuum device is related to the sum of the flows from equipment air leakage, inert-gas blankets provided for safety or product decomposition reasons, dissolved gases in liquid or solid feeds, and gases generated because of chemical decomposition or reaction. The emissions resulting from the leak rate and inert gases added for safety considerations are quite significant when the total emission flow is to be estimated. Normally, gases dissolved in liquids and solids and those evolved because of chemical decomposition are insignificant. Reactions in which gases are formed may be significant but are highly specific and are discussed in other reports.

The VOC concentration in vacuum device emissions varies from almost zero to almost 100 mole % and is primarily a function of the specific chemicals being processed, their vapor pressures, and their water solubilities.

Control devices to be applied to vacuum source emissions should have low pressure drops and not be affected by high levels of water vapor. Existing control devices are generally aftercondensers (with or without refrigeration), scrubbers, adsorbers, and combustion devices such as flares, boilers, or thermal oxidizers.

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APPENDIX A

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LIST OF EPA INFORMATION SOURCES

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REPORT 5

UPSET RELEASES

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ABBREVIATIONS AND CONVERSION FACTORS

EPA policy is to express all measurements used in agency documents in metric units. Listed below are the International System of Units (SI) abbreviations and conversion factors for this report.

To Convert From	To	Multiply By
Pascal (Pa)	Atmosphere (760 mm Hg)	9.870 X 10^{-6}
Joule (J)	British thermal unit (Btu)	9.480 X 10^{-4}
Degree Celsius (°C)	Degree Fahrenheit (°F)	(°C X 9/5) + 32
Meter (m)	Feet (ft)	3.28
Cubic meter (m^3)	Cubic feet (ft^3)	3.531 X 10^1
Cubic meter (m^3)	Barrel (oil) (bbl)	6.290
Cubic meter (m^3)	Gallon (U.S. liquid) (gal)	2.643 X 10^2
Cubic meter/second (m^3/s)	Gallon (U.S. liquid)/min (gpm)	1.585 X 10^4
Watt (W)	Horsepower (electric) (hp)	1.340 X 10^{-3}
Meter (m)	Inch (in.)	3.937 X 10^1
Pascal (Pa)	Pound-force/inch^2 (psi)	1.450 X 10^{-4}
Kilogram (kg)	Pound-mass (lb)	2.205
Joule (J)	Watt-hour (Wh)	2.778 X 10^{-4}

Standard Conditions

68°F = 20°C

1 atmosphere = 101,325 Pascals

PREFIXES

Prefix	Symbol	Multiplication Factor	Example
T	tera	10^{12}	1 Tg = 1 X 10^{12} grams
G	giga	10^9	1 Gg = 1 X 10^9 grams
M	mega	10^6	1 Mg = 1 X 10^6 grams
k	kilo	10^3	1 km = 1 X 10^3 meters
m	milli	10^{-3}	1 mV = 1 X 10^{-3} volt
μ	micro	10^{-6}	1 μg = 1 X 10^{-6} gram

I. INTRODUCTION

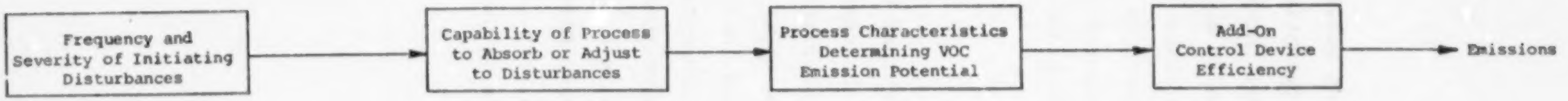
A. DEFINITION

Upset emissions as used in this report are defined as intermittent volatile organic chemical (VOC) emissions that occur when normal process operation or the operation of emission control devices is disturbed by abnormal internal or external conditions or events. Intermittent emissions that normally occur during planned and scheduled startup/shutdown operations at predictable frequencies and rates and for predictable time intervals are considered as normal process emissions; however, abnormal emissions caused by unanticipated conditions or events occurring during scheduled startup/ shutdown operations are considered to be upset emissions.

B. ELEMENTS THAT DETERMINE VOC EMISSIONS

The total quantity of VOC upset emissions from a process is determined by the frequency and duration of initiating disturbances or causes, by the capability of the process to absorb or adjust to disturbances, by the characteristics of the process that determine the quantity of VOC discharged when an upset does occur, and by the efficiency of terminal control devices when such controls are applicable. Table I-1 illustrates the relationship between the elements described and itemizes (1) the most common sources of initiating disturbances, (2) the process factors that affect the potentiality of an upset, and (3) the characteristics that determine the potential for VOC emissions when upsets do occur. Item (1) is discussed in detail in Sect. II, item (2) in Sect. III, and item (3) in Sect. IV. Applicable emission controls are discussed in Sect. VI.

Table I-1. Elements Determining the Frequency and Severity of Process Upsets and the Resulting Quantity of Emissions


Frequency and Severity of Initiating Disturbances
Capability of Process to Absorb or Adjust to Disturbances
Process Characteristics Determining VOC Emission Potential
Add-On Control Device Efficiency
Emissions

Initiating Causes	Factors Affecting Upset Potential	Emission-Controlling Process Characteristics
External	Holdup	Properties of materials (feeds, products, by-products)
Utilities interruption	Parallel or single-train equipment	Physical properties
Electrical power	Intermediate storage	Vapor pressure
Steam	Emergency equipment	Chemical properties
Cooling water	Installed spare equipment	Mutual reactivity
Compressed air	Controls	Heats of reaction
Feed sources	Response time	Potential for reactions that increase gas volume
Flow disturbance	Stability	Process/system properties
Composition change	Fail-safe features	Volume
Consuming units	Operation	Throughput
Flow interruption	Procedures	Pressures
Internal	Training	Temperatures
Rotary equipment outages		State (gas, liquid)
Compressors		Inert-gas flow
Pumps		
Miscellaneous		
Flow restrictions		
Piping		
Equipment		
Control problems		
Instruments		
Operator error		
Direct material release		
Rupture/leaks		
Pressure-relief device failure		

II. INITIATING CAUSES

A. GENERAL

Process upsets may be initiated either by external occurrences (e.g., interruptions or variations in utilities, raw material supplies) or by disturbances within the process itself (e.g., mechanical equipment failure, control malfunctions). Specific causes are discussed in detail in the following sections.

Table II-1 summarizes the common initiating causes, the processes responsible, and the frequency of upsets in each category that were reported by the SOCMI in Texas State Region 7 (Houston area) to the Texas Air Control Board* (TACB) for the periods of January—April 1978 and May—December 1979. As approximately 30 to 50% of the total SOCMI production occurs within this region, the predominant sources and causes shown are probably reasonably representative of the major industry sources of upset emissions.

The reported incidents that resulted in the release of only such inorganic pollutants as SO_2, NO_2, and inorganic particulates were excluded; however, those incidents that resulted in the release of particulate emissions were included when the emissions were caused by incomplete combustion (in flares, incinerators, or boilers) of VOC released as a result of process upsets. Since upset incidents are required to be reported only when emissions are potentially in excess of regulatory requirements, many upset incidents were probably not reported because the VOC released was satisfactorily controlled by terminal control devices.

B. EXTERNAL CAUSES

1. Interruptions in Utilities

a. Electrical Power—Electrical power failure is the most significant source of externally caused process upsets. In addition to electrical power being required for process pumps, process gas compressors, instruments, controls, and

---

*The state of Texas requires that those incidents which may result in emissions in violation of regulations be reported.

Table II-1. Initiating Causes of Upset Emissions Reported to TACB by Organic Chemical Plants in Texas Region 7*

	Number of Incidents for Sources Listed													
	Internal Sources								External Sources					
Process	Compressor Outage	Other Equipment	Equipment, Line Rupture, Fire	Leakage	Plugging/Freezeup	Control Malfunction	Operator Error	Relief-Valve/Rupture-Disk Failure	Electrical Power	Steam and Cooling Water	Raw Materials (Flow/Composition)	Consuming Units/Off-Spec. Product	Not Identified	Total
Entire plant				1					2					3
Acetaldehyde				1									1	2
Acetic acid						1							1	2
Acetone											1			1
Acetylene						1							8	9
Alcohols (unspecified)	1												1	2
Acrylates		1				1	1	1					2	6
Acrylonitrile	1												1	2
Adipic acid														
Allyl chloride				1										1
Butadiene			1	1				1		1			4	8
n-Butanol					1									1
Carbon tetrachloride				2	1	1			1				2	7
Chlorinated hydrocarbons (unspecified)	3	2	1	1		5	5	1	4	1			22	45
Cyclohexane		1	2											3
Epoxy								1						1
Ethanol	1										1		6	8
Ethylene (olefins)	60	2	6	3	7	13	1	11	4	8	1	4	39	159
Ethylene dichloride (EDC)			2			2							1	5
Ethylene diamine (EDA)					1	3							1	5
Ethylene oxide		2		1	1									4
Ethylene glycol													1	1
Ether						1								1
Glycerin								1					2	3
Isopropanol				3					1					4
Maleic anhydride		2		2									1	5
Oxo process						2	1							3
Propylene oxide			1										2	3
Phenol/acetone			1			1							1	3
Polyethylene	3	4		1	1			1	2	1	3		6	22
Polypropylene	4					1			2	1			1	9
Polyvinyl chloride (PVC)			1	1		2	3	9	2		1		4	23
Styrene/ethyl benzene		2							1					3
Vinyl acetate	2	1											3	6
Vinyl chloride (monomer)	3	7	1	5		8	6	9	3	1			9	52
Xylenes						1							1	2
Total	78	24	16	23	12	43	17	35	22	13	7	4	120	414

*Includes the incidents that occurred from January—April 1978 and from May—December 1979.

lighting, a plant-wide electrical power failure may result in outages of cooling water, steam, and compressed air, which require electrically operated pumps, compressors, and controls. Because of the widespread effects of plant-wide electrical power outages and because they can occur instantly and frequently without warning, the resulting process upsets are usually severe. Without adequate protective measures, catastrophic incidents such as fires, explosions, and equipment rupture can result. Such critical situations are normally avoided by provisions for alternative emergency power supplies to essential equipment and/or other emergency alternatives (e.g., alternative steam-driven pumps, supplies of emergency cooling water in overhead storage tanks).

b. Steam—Plant steam required in large, multiprocess plants is usually primarily supplied by a number of centrally located boilers but is frequently supplemented by steam generated by the recovery of heat from various process sources, such as exothermic reactions, process furnaces, and incinerators. Because of the common multiplicity of sources and uses, steam supplies are generally less subject to sudden and total outages than are electrical power supplies; however, fluctuations in steam supply pressure, which are relatively common, can cause significant process upsets. Common steam-consuming equipment that is vulnerable to upsets includes turbines, compressors, pumps, and jet ejectors, heated reactors, evaporators, preheaters, feed vaporizers, and distillation column reboilers.

c. Cooling Water—Interruptions in the supply of cooling water are usually caused by either the failure of cooling water pumps or cooling tower fans or by electrical power outages and can result in severe process upsets. Critical requirements for cooling water may include the control of exothermic reactions and the quenching of high-temperature effluent streams from process furances. Distillation column condensers, compressor interstage and after-coolers, and refrigeration cycle condensers are commonly vulnerable to the loss of cooling water, with the subsequent release of VOC likely.

d. Compressed Air—Interruptions in compressed-air supplies usually result from outages of air compressors either because of mechanical problems or because of electrical power or steam outages. Common uses of compressed air include oxidation reactions and pneumatic instruments and controls. Although compressed-air requirements for pneumatic instruments are relatively small compared to direct-process requirements, the consequences of interruption in the supply are usually severe.

2. Disturbances in Feed Supplies

a. General—Process upsets can result both from interruptions or variations in feed supply rates and from variations in feed composition or purity. In general process upsets resulting from variations in feed flow rates are more likely for gaseous feed streams than for liquids or solids because the storage of large quantities of gases is usually more difficult and costly. Frequently there is little or no intermediate storage of gaseous materials between producing and consuming units, and an upset in a producing unit may result in an almost immediate corresponding disturbance in the consuming units.

Variations in feed composition or purity usually occur more gradually than rate variations; however, the time required to re-establish normal stream compositions in both the producing and consuming units may be extensive, and significant quantities of off-specification materials may be vented when gaseous materials are produced.

3. Disturbances in Product Consumption

a. General—A cutback or shutdown of a unit that consumes gaseous materials can cause an upset in the feed producing unit if the unit that suddenly goes down is one that consumes a large part or all of the producing unit's output. As is discussed in Sect. II-B.2, intermediate storage capacity for gaseous materials is frequently very limited, and when a consuming unit suddenly reduces consumption, the producing unit must either make a corresponding cutback or vent its output until normal operation can be re-established. Continued normal production rates with the venting of output from the producing unit usually occurs only for short periods of time (i.e., a short-duration cutback by the consuming unit or until the output of the producing unit can be reduced).

C. INTERNAL CAUSES

1. Rotating Equipment Outages

a. Compressors and Blowers—The outage of compressors is the most significant single cause of upsets from the standpoint of the number of incidents reported and from the standpoint of the quantity of VOC that is vented. Compressors are particularly vulnerable to upset situations because maintenance or repair requirements are generally relatively high; operating problems, when they develop, frequently require immediate shutdown; installed spare capacity is usually minimal due to high capital costs; and temporary storage of the process gas (at compressor suction conditions) is usually not feasible.

b. Pumps—Pump failure can be a significant cause of direct process upsets, as well as the initiating cause of interruptions in essential utilities (e.g., failure of cooling water pumps, boiler feedwater pumps, and boiler fuel oil pumps) and of interruptions in emission control devices.

c. Miscellaneous Mechanical Equipment—The failure of other items of mechanical equipment, such as agitators, vacuum pumps, solids transfer equipment, is less significant as causes of upsets with the potential for VOC emission.

2. Restrictions in Equipment and Piping

A significant cause of process upsets is the sudden development of restrictions to flow (plugging) or heat transfer in piping and equipment. Most of these restrictions occur when solids are formed or are deposited in piping and equipment that normally contain liquid or gaseous materials. Frequent causes of such solids formation include the partial pyrolysis of organic compounds, polymerization, precipitation of contained inorganic compounds that have limited solubility, accumulation of ice or hydrates in low-temperature equipment caused by abnormal concentrations of water in feed streams, and freezing of piping and equipment subjected to abnormally low atmospheric temperatures.

3. Control Problems

a. General—Control malfunction and improper operating performance can directly cause process upsets. Also, controls and operator performance can affect the severity and duration of upsets resulting from other causes. The importance of controls and operator response in minimizing the effects of process disturbances is discussed in more detail in Sect. III-E.

b. Process Instrumentation and Control—An automatic process control system usually consists of a primary sensing element, a measuring element, the controller proper, a power unit, and a final control element. Although process upsets can result from malfunctions of any of the control elements, problems with primary sensing elements and final control elements are the most frequent ones.

In addition to problems directly attributable to the control elements, control malfunctions may be caused by interruptions or fluctuations in power supplies to the control systems. Control systems are almost always either electrically or pneumatically powered (or a combination of the two) and therefore depend on an uninterrupted supply of electrical power or compressed gas (usually dry compressed air). Consequently, the reliability of power sources for control systems is of primary importance.

c. Operating Personnel—Operator error or inattention is a frequent cause of process upsets. Most operating errors occur during periods of nonroutine plant operation (startups, shutdowns, maintenance, upsets from other causes). Lapses or errors in communication are frequent sources of operational errors.

4. Direct Material Releases

a. General—The development of severe leaks, the rupture of process equipment and piping, and the failure or malfunctioning of pressure-relief devices are significant sources of VOC emissions. In addition to the immediate and direct release of VOC such incidents may also cause significant process upsets that may result in additional emissions.

b. Severe Leaks—Major leaks in piping and equipment that occur suddenly and that require immediate isolation of the affected parts from adjoining piping or equipment are considered as process upset causes and are sources of upset emissions. Emissions from leaks that are predictable and that occur either continually or with high frequency but at low rates and are therefore considered to be fugitive emissions. Fugitive emissions are discussed in a separate report.[1]

Major leaks most frequently result from the failure of welds, gaskets, flanges, or other fittings or from the failure of pump and compressor mechanical seals and packing.

c. Rupture of Equipment or Piping—Sudden rupture of equipment and piping, explosions, and fires are considered to be catastrophic incidents. Although they are actually upset incidents, they are considered to be outside the scope of this report because the emissions are usually of secondary importance compared to safety considerations; the incidents are very infrequent; the resulting emissions are not predictable; and the control of the emissions is not usually feasible.

d. Failure of Pressure-Relief Devices——The premature activation of relief devices can cause significant process upsets. The normal activation of pressure-relief devices, which occurs when normal operating pressures are exceeded, is usually the result of process upsets and not a primary cause; however, emissions resulting from the activation of pressure-relief devices when the releases occur at normal operating pressures or below the set or design pressures of the devices are considered to be upset emissions.

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[1] D.G. Erikson and V. Kalcevic, IT Enviroscience, Fugitive Emissions (September 1980) (EPA/ESED report, Research Triangle Park, NC).

III. CHARACTERISTICS THAT DETERMINE THE CAPABILITY OF PROCESSES TO ABSORB OR ADJUST TO DISTURBANCES

A. GENERAL

This section covers some of the characteristics of processes that determine the severity and duration, and ultimately the potential for VOC emissions, of upsets resulting from the initiating disturbances discussed in Sect. II.

B. SYSTEM HOLDUP

The holdup of a process system is the ratio of volume or capacity to the material throughput rate. Generally, the greater the holdup of the system the less sensitive it is to minor fluctuations or deviations in process parameters. However, once an upset occurs, the duration of the upset is usually greater in higher-holdup systems. Systems or equipment in which material is in the liquid phase generally have greater holdup than vapor-phase systems.

C. MULTIPLE PARALLEL EQUIPMENT VS SINGLE-TRAIN EQUIPMENT

The trend in many of the SOCMI plants that produce large volumes of organic chemicals by continuous processes has been toward the use of very large equipment and single process trains and away from the use of multiple, parallel items of equipment. Large single-train systems often have a number of distinct advantages over smaller, parallel systems. The primary advantage is generally lower unit costs. Unit capital costs generally decrease as capacity is increased. Most instrumentation/control requirements (not including control valves) and the resulting costs are virtually independent of production capacity. Operating labor costs are generally virtually independent of equipment capacity, and maintenance costs are also usually substantially lower for one large item of equipment than for two or more smaller items with the same total capacity.

Upsets resulting from the internally caused disturbances discussed in Sect. II are generally more severe and of greater duration with single-train processes than with processes that utilize multiple, parallel equipment, with the severity and duration of upsets tending to diminish as the number of parallel equipment items increases. The number of internally caused disturbances will, however, increase because of the greater number of possible sources. The net effect is usually a lower potential for upset emissions from systems with parallel equipment.

The use of parallel systems will usually not reduce the potential for upset emissions caused by external disturbances (e.g., electrical power failure) because they will usually simultaneously affect all parallel systems. This is not necessarily true when parallel items are supplied by separate utility sources such as separate electrical power supplies, or when one compressor is steam-driven and a parallel compressor is electrically driven.

D. INTERMEDIATE STORAGE CAPACITY

A common characteristic of most continuous processes is the tendency for an upset in one operation to be rapidly transmitted to other operations in the process or to other process units within an integrated plant that either supply the affected unit with feed material or consume products from it. Frequently the effects of the secondary upsets are more severe and of greater duration than the effects of the initial disturbance. The severity of the upset can therefore be minimized if its effect can be confined to the initially disturbed operation.

The primary means of preventing or minimizing the effects of secondary disturbances is by providing adequate storage capacity for intermediate feed materials or products, permitting the adjacent operations or units to continue to operate in a normal fashion until normal operation in the affected unit is restored or at least providing the secondary operations with sufficient time for orderly shutdowns or cutbacks.

The cost of providing intermediate-storage capacity for a specific application must be balanced against the potential for interruption and the severity of the effects of an interruption. The intermediate storage of liquids is generally more feasible than that for gases; however, gas storage may be provided by atmospheric gas holders or by condensing the gases at elevated pressure and/or low temperature (refrigeration), with subsequent storage as liquids.

Underground salt domes are commonly used for the storage of large quantities of ethylene and propylene in the gaseous state at elevated pressures. Such underground storage provides sufficient capacity to permit the balancing of ethylene production and consumption during relatively long-term shutdowns required for major maintenance to the producing/consuming units. Salt-dome storage is limited primarily to the Gulf Coast.

E. EMERGENCY/SPARE EQUIPMENT

1. General

Because of the capital requirements for equipment that is used only a small fraction of the time the installation of emergency and/or other spare equipment can usually be justified only for critical areas in which sudden outages can cause severe or catastrophic occurrences or where poor reliability of equipment and the need for frequent maintenance are a problem. Some of the situations in which emergency/spare equipment is commonly provided are discussed in this section.

2. Electrical Power

Since the total outage of electrical power can frequently result in critical or even catastrophic situations, most plants have emergency electrical power supplies for critical equipment. The normal power supply to most processing plants is from public utility sources. The public power companies sometimes provide processing plants with power supplied from two totally separate generating sources.

When generators located in the processing plant provide the emergency power supply, they are usually sized to provide power to critical equipment only and are not adequate to supply all normal plant requirements. Items commonly supplied from plant emergency power sources include critical process compressors and pumps, cooling-water pumps, boiler-feed-water pumps, cooling-tower fans, air compressors that supply pneumatic instruments and controls, electrically powered instruments, control-room lighting, and water pumps required for fire fighting purposes. Emergency power supply systems are generally not designed to prevent all process upsets from occurring but to prevent serious or catastrophic upset incidents.

3. Cooling Water

In addition to emergency power supplies provided for cooling-water pumps critical supplies of cooling water may also be protected with alternative steam-driven spare pumps or with overhead water storage tanks that will provide cooling long enough to shut down such critical equipment as exothermic reactors or high-temperature pyrolysis furnaces. When closed cooling water systems using forced-draft cooling towers are used to provide essential cooling water, the cooling-tower fans may also be provided with emergency electrical power.

4. Steam

For critical steam requirements standby or emergency boilers may be provided. Control systems that automatically shut off the steam supplies to noncritical users in the event of partial steam supply outages (e.g., loss of one of two or more boilers) can usually prevent the loss of supply or insufficient pressure for critical uses.

5. Compressed Air

As is discussed in Sect. III D-2, when compressed air is needed to operate pneumatic instruments and controls, the air supply is safeguarded with spare compressor capacity and an emergency power supply.

6. Installed Spare Process Equipment

Spare equipment items are frequently installed in parallel with the items that they are intended to replace, with the necessary valves provided to permit rapid diversion to the spare equipment.

The primary advantage of providing installed spares is that the upsetting effects caused by equipment outages can be minimized. Frequently, if the outage can be anticipated and the switch to the spare item is made smoothly, no significant process upset will occur.

Installed spares are frequently provided for pumps in critical service or in services where outages are frequent because of high maintenance requirements. Because of generally much higher capital costs for compressors than for pumps the installation of spare compressors is not as common except in critical services. The installation of spare equipment can generally be more easily justified if the spare item can be used as a replacement for any one of several items (i.e., multiple, parallel systems) rather than as a replacement for a single item.

F. PROCESS CONTROLS

The effectiveness of automatic controls can have significant impact on the capability of processes to adjust to certain disturbances without serious upsets resulting. A detailed discussion of instrumentation and process control is outside the scope of this report; however, several of the most significant factors are discussed briefly below:

1. Response Time

The elapsed time between the initiation of a process disturbance and the application of corrective action by an automatic control system can have a significant impact on the control stability and the severity of process upsets caused by disturbances. Control loops that have extensive time lag tend to be unstable, with resultant significant cycling of the controlled variables. The primary sources of time lag are the times required for the controlled variable to respond to the disturbance, for the sensing element to detect a change in the controlled variable, and for the control system to apply corrective action. Time lag caused by the control system itself is usually minor compared to the time lag caused by delays in process response.

2. System Holdup

The effects of holdup are discussed in Sect. III-B.

3. Fail-Safe Features

In the design of automatic controls consideration must be given to the consequences of the malfunctioning or total failure of the sensing elements. The options normally available when failures occur are that the final control element will assume the fail-open or fail-closed position or in some cases will maintain the same position it was in at the time that the failure occurred. The option selected will normally be the one that best guards against the development of hazardous situations. If failure of the control system does not create a potentially hazardous situation, the fail-safe position selected is normally the one that minimizes the severity of any resulting upset.

G. OPERATION

Most of the SOCMI plants that produce the bulk of organic chemicals utilize continuous processes that rely primarily on automatic controls during normal operation; however, the ability of process operators and supervisory personnel to respond quickly and effectively during startups, shutdowns, or upsets largely determines the efficiency with which normal operation is re-established and the corresponding severity and duration of upsets. Important aspects of effective operation during abnormal situations include effective communication, preplanned procedures to be used during abnormal situations, and advance training in diagnosing the causes of abnormal situations and applying the correct procedures.

IV. PROCESS CHARACTERISTICS THAT DETERMINE THE POTENTIAL FOR VOC UPSET EMISSIONS

A. GENERAL

The frequency and severity of the initiating disturbances (Sect. II) and the characteristics that determine the capabilities of processes to absorb or adjust to disturbances (Sect. III) determine the frequency, duration, and severity of the resulting process upsets; however, process upsets, alone, will not necessarily result in VOC emissions. The potential for VOC emissions during process upsets is determined by the process characteristics discussed in this section. An assessment of these characteristics is probably of greater value for identification of processes with very low potential for VOC upset emissions than for estimation of the quantities of emissions.

B. CHARACTERISTICS OF RAW MATERIALS, INTERMEDIATES, PRODUCTS, AND BY-PRODUCTS

1. Physical Properties

The vapor pressure is the most significant physical property of an organic process material from the standpoint of its potential for VOC emission. Figure IV-1 shows the atmospheric boiling points (vapor pressure = 760 mm Hg) of groups of organic compounds that are frequently present in the SOCMI processes. The compounds with boiling points above ambient temperatures are not normally released as VOC emissions unless they are transported by a carrier gas, are released as vapor at temperatures above their boiling points, or are discharged as liquids and subsequently evaporate. The potential for VOC emissions from processes containing only compounds with low vapor pressures is generally much less than that for processes containing compounds with higher vapor pressures.

2. Chemical Properties

Important chemical properties include the mutual reactivity of process materials, the exothermic heats of reaction, and the potential for volumetric increases resulting from increases in the number of moles of gas present. These properties are significant not only for the organic compounds present but also for the inorganic compounds, as well. Heat evolved from the reaction of both organic and inorganic compounds can cause the temperatures of organic gases to

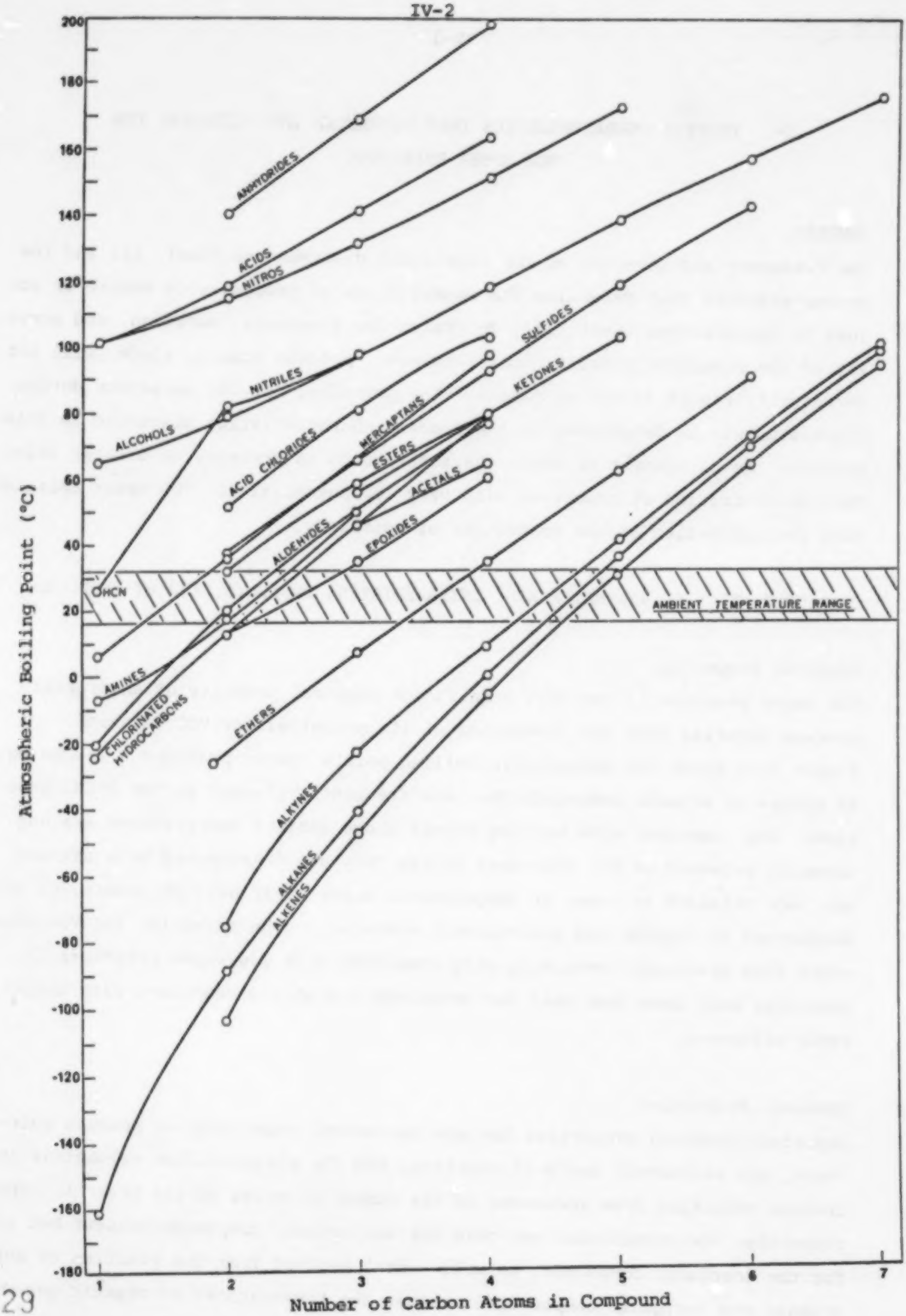

Fig. IV-1. Boiling Point as a Function of Carbon Atoms in Compound

increase, thereby causing the pressures to increase. Similarly the generation of inorganic gases such as CO_2 can cause the pressure to increase and ultimately lead to the release of VOC.

C. PROCESS/SYSTEM CHARACTERISTICS

1. Volume/Throughput

The volume of equipment and piping and the throughput rates (combined with VOC concentration) determine the quantity of VOC present in the system during an upset and therefore establish the upper limit on the emissions that can occur as the result of a process upset.

2. Pressure

Operations that occur at elevated pressure generally have greater potential for upset emissions than operations conducted at or below atmospheric pressure. The potential for emissions increases with the pressure-volume energy that can be released during an upset.

3. Temperature

The effects of temperature on the potential for upset emissions are not as clearcut as pressure effects are. Both high- and low-temperature operations may have significant potential for upset emissions. Organic compounds whose vapor pressures are not significant at lower temperatures may be present as vapor in significant concentrations at elevated temperatures to present a potential for VOC emissions. On the other hand low-temperature operations, in which organic compounds with low boiling points are normally maintained as liquids, are susceptible to upset situations that result in their vaporization. In both cases emissions of VOC are most apt to occur in upset situations in which the normal rate of heat addition is excessive; or, if heat is normally removed, the rate of heat removal is less than normal, causing either abnormal temperature increases or abnormal vaporization of liquid.

Operations in which low-boiling organic compounds are maintained as liquids by refrigeration are particularly susceptible to upset emissions caused by mechanical equipment (compressors) failure or power outages.

4. Carrier Gas Flow

Normal process emissions frequently result from the venting of non-VOC gases that were introduced as feed impurities (e.g., nitrogen in air oxidation processes) or were formed as by-products. The vented gas will frequently contain some VOC, the concentration being dependent on process conditions and on the effectiveness of control devices.

Processes that vent significant quantities of carrier gas are often vulnerable to process upsets, and relatively small upsets in process or control device conditions can cause significant increases in the VOC concentration of the vented gas.

V. EMISSIONS

A. INTRODUCTION

Upset emissions are estimated to account for approximately 4—11 million lb annually, or only about 0.3—0.7% of the total VOC emissions from the SOCMI in 1978. Estimates of upset emissions, together with the corresponding initiating causes, for 32 significant organic chemicals produced in TACB region 7 are given in Table V-1. Estimates of upset emissions for the total SOCMI are given in Table V-2. The estimates given in Table V-2 were obtained by prorating the estimates from Table V-1 (TACB region 7) to total industry production and from separate estimates of emissions caused by ethylene plant compressor outages (not included in Table V-1). Calculations of ethylene plant compressor-outage emissions are given in Appendix A.

The estimates of upset emissions given in Tables V-1 and V-2 are based on very limited data and should be considered as order-of-magnitude estimates only. The primary conclusion that may be drawn from those estimates is that upsets are a relatively minor source of VOC emissions compared to fugitive, storage, handling, and normal process emissions (see Appendix A, p A-6, for calculations).

B. ESTIMATION CRITERIA

Upset emissions are difficult to measure because they are intermittent and because emissions from specific sources are generally unpredictable as to frequency, rate, and duration. The estimates for the industry were developed primarily from data on upset incidents reported to the Texas Air Control Board (TACB) by the SOCMI plants located in TACB region 7 (Houston area) from January— April 1978 and from May—December 1979. These periods were selected because specific information from the upset reports received by TACB during those periods had been incorporated in a computerized data collection system and were available in summary form. These summary data were supplemented with additional information extracted from the relevant report logs maintained by TACB during the periods.

Although the geographic area encompassed by TACB region 7 represents only a small fraction of the total area in the United States, more than one-third of

Table V-1. Estimated Annual Upset Emissions from Organic Chemical Plants in Texas Air Control Board Region 7[a]

Initiating Cause[b]	Number of Incidents	Average VOC Emissions per Incident (lb)	Total Estimated Emissions[c] (M lb)
Miscellaneous compressor outages[c] (ethylene plant compressors not included)	18	3200	57.6
Miscellaneous mechanical equipment	24	720	17.3
Major leaks	23	5700	131.1
Restrictions (plugging/freezeup)	12	900	10.8
Control malfunction	43	600	25.8
Operator error	17	1400	23.8
Relief-device failure	35	4460	156.1
Electrical power failure[d]	22	2680	59.0
Other causes	144	1160	167.0
Total	338		648.5

[a] Estimates were developed primarily from data on upset incidents reported to the Texas Air Control Board by the SOCMI plants located in TACB Region 7 (Houston area) from January—April 1978 and from May—December 1979.

[b] Emissions resulting from major accidents, including the rupture of major equipment, fires, and explosions, are not included in this table nor in the estimate of total upset emissions.

[c] Estimated emissions resulting from 60 ethylene plant compressor outages are not included in this table but were estimated separately to develop Table V-2.

[d] Emissions estimated from power failures that were reported by TACB were for relatively minor or localized power outages. No emission estimates were given for three plant-wide power failure incidents reported during this period.

Table V-2. Estimated Annual Upset Emissions from SOCMI Plants in the U.S.[a]
(M = 1000)

Source	Current VOC Losses from Processes (m lb)	Percent Currently Controlled	Emissions After Flares (m lb)		Estimated Reduction Attainable if Currently Uncontrolled Vents from Relief Devices are Flared (m lb)	
			With 90% Control Efficiency[b]	With 98% Control Efficiency[b]	With 90% Control Efficiency[b]	With 98% Control Efficiency[b]
Ethylene plant compressor outages	82,100	98	9690	3250	1480	1610
Major leaks	390	0	390	390	0	0
Other upset sources	1,550	50	850	790	700	760
Total	84,040		10,930	4430	2180	2370

[a] Estimates were based on upset incidents reported by plants in TACB region 7 and on the following criteria:

1. An estimated 50% of ethylene production and 30% of other SOCMI production is in TACB region 7.
2. Emissions are proportional to production rates.
3. Ethylene plant compressor-outage emission calculations given in Appendix A.
4. Emissions from flares were estimated for flare efficiencies of 90% and 98%.
5. Ethylene plant compressor-outage emissions were assumed to be entirely discharged to flares.
6. 50% of other emissions from relief devices were assumed to be discharged to flares.

Actual emissions may be significantly greater because estimates of emissions resulting from total plant power-failure incidents are not included and because some upset incidents may not have been reported if the emissions were flared smokelessly.

[b] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using standard fuels. Efficiencies used are for tentative comparision purposes.

the total quantity of chemicals produced by the SOCMI and more than half of the ethylene and ethylene-based chemicals are produced in this region. It was therefore concluded that a reasonable order-of-magnitude estimate of upset emissions for the entire SOCMI could be obtained by prorating the upset emissions estimated for TACB region 7 to the total, according to the relative quantities of organic chemicals produced.

The information available from the TACB upset incident reports was quite complete with respect to upset sources, initiating causes, and duration of upsets. Information on the estimated quantities of VOC emitted was not included in many of the reports, probably because in most cases the quantities were not known. The estimated emissions shown in Table V-1 were determined by averaging the estimates for those sources that were included in the upset-incident reports to TACB.

Estimates of upset emissions caused by ethylene-plant compressor outages were not generally included in the upset information reported to TACB. The estimates of emissions from these sources were developed from the number of ethylene-plant compressor outage incidents reported to TACB (Table II-1), from an estimate of the average material lost per compressor outage (based on the experience of one large ethylene manufacturer[1]), and from estimates of the average efficiency of the final emission control devices (flares). (See Appendix A)

Because of the differences in estimating procedures and source data for ethylene plant compressor outage emissions and other upset emission sources, the separate estimates are not directly comparable. The separate estimates were primarily used to develop order-of-magnitude estimates of total upset emissions from the SOCMI.

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[1] R. P. Paveletic, A. C. Skinner, and D. Stewart, "Why Dual Ethylene Unit Compressors?" Hydrocarbon Processing 55(10), 135—138 (1976).

VI. APPLICABLE CONTROLS

A. GENERAL

Flares are the devices most frequently used for the terminal control of upset emissions. Because upset emissions are usually relatively infrequent and of short-term duration and because they can occur at extremely high and variable rates, incineration, carbon adsorption, gas absorption, etc., are less frequently applicable.

Often the most effective methods of reducing upset emissions are by eliminating or reducing the frequency or severity of the initiating disturbances that cause the upsets (Sect. II) or by improving the capability of the process to absorb or adjust to disturbances (Sect. III).

Control methods are generally not applicable when emissions are caused by the direct release of VOC resulting from the unpredictable and sudden rupture or severe leakage of piping or equipment; however, if such incidents occur frequently, a need is indicated for improvement in process design, operating and safety procedures, equipment and piping specifications, or preventive maintenance procedures.

B. ADD-ON CONTROLS

1. Flares

Elevated flares that utilize steam injection to provide smokeless emissions are most commonly used to control upset emissions. Additional information on flares is presented in a separate control device evaluation report.[1]

Because scrubbing devices are not adaptable to flares, flares are not normally suitable for the control of emissions that contain significant concentrations of inorganic acids, halogens, sulfur, or other inorganic components that will cause objectionable emissions.

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[1] V. Kalcevic, IT Enviroscience, Control Device Evaluation. Flares and the Use of Emissions as Fuel (in preparation for the EPA, ESED, Research Triangle Park, NC).

2. Other Add-On Controls

Flares may not be a suitable upset emission control method in some situations and the use of other add-on controls (e.g., incineration, gas absorption) may be required. Because the rapid relief of process equipment during upsets is frequently necessary to prevent potentially hazardous situations, safety and loss prevention must be a major consideration in the selection of upset emission controls.

C. ELIMINATION OF INITIATING DISTURBANCES

1. General

The common initiating disturbances that cause upset emissions and the methods of reducing the number and severity of such disturbances are discussed in Sects. II and III.

D. IMPROVEMENTS IN CAPABILITY TO ABSORB OR ADJUST TO DISTURBANCES

1. General

The factors that commonly determine the capabilities of processes to absorb or adjust to disturbances are discussed in Sect. III.

The retrofitting of single-train equipment to dual or multiple, parallel systems is usually not feasible in existing plants; however, the impact of single-train vs parallel equipment on upset emissions can be considered in the design of new process facilities.

VII. ASSESSMENT

A. SUMMARY

Upset emissions are defined as intermittent VOC emissions that occur when normal process operation is disturbed by abnormal internal or external conditions or events, excluding emissions that normally occur during scheduled startup, shutdown, and maintenance periods. Upset emissions are relatively minor compared to the other sources of VOC emissions (i.e., normal process vents, fugitive, and storage and handling), accounting for only about 0.3 to 0.7% of the total and the impact of controlling those sources that are feasible to control but are currently uncontrolled would be relatively minor. An estimated reduction of about 2—2.5 million lb of VOC/yr is projected if emissions from all relief devices that are currently vented without control were flared.

The most significant sources of upset emissions are the processes that produce and consume ethylene, with upsets caused by ethylene plant compressor outages predominating.

The quantities of VOC that are released as upset emissions by specific processes are determined by the frequency and severity of initiating disturbances; the capability to adjust to disturbances; the emission potential when upsets do occur; and the effectiveness of terminal control devices.

Flares are the control devices primarily used for the terminal control of upset emissions. The general characteristics of upset emissions (i.e., intermittent, unanticipated, infrequent, high and widely varying rates) generally exclude other types of terminal control devices.

B. DATA ASSESSMENT

Because of their eratic nature upset emissions are very difficult to measure, and very little direct emission data are available.

The conclusions presented in this report are based on order-of-magnitude estimates of emissions for the total SOCMI, which were developed primarily from upset-incident reports submitted to Texas Air Control Board (TACB) from the

SOCMI plants in region 7 (Houston area); estimates of material losses resulting from ethylene-plant compressor outages, based on the reported operating experience of one large ethylene manufacturer; and estimates of the degree of control and the VOC removal efficiency of the flare systems currently used to control compressor outage emissions from existing ethylene plants.

APPENDIX A

UPSET EMISSION ESTIMATE CALCULATIONS

UPSET EMISSION ESTIMATE CALCULATIONS

I. SUMMARY OF CRITERIA FOR EMISSION ESTIMATES

Following is a summary of the criteria used as the basis for the estimates of upset emissions caused by ethylene plant compressor outages.

1. The average material loss per compressor outage (trips and checks only) from a plant producing 1 billion lb of ethylene per year is 1,800,000 lb with single compressor trains and 135,000 lb with dual trains (Table V-2).
2. Material losses caused by compressor outages are proportional to ethylene production.
3. The average capacity of plants using gas liquid feedstocks (primarily ethane and propane) is 513.6 million lb of ethylene per year.[1]
4. The average capacity of plants using heavy-liquid feedstocks (primarily naphthas and gas oils) is 1107.5 million lb of ethylene per year.[1]
5. Distribution of single and dual compressor trains:

   Plants using ethane/propane (E/P) feedstocks, 50% with single compressor trains; 50% with dual trains.[1]

   Plants using naphtha/gas-oil (N/G) feedstocks, 90% with single compressor trains; 10% with dual compressor trains:[1]

6. Distribution of plants using E/P and N/G feedstocks:[1]

	Number of Plants	% of Total
Plants using E/P feedstocks	39	68.4
Plants using N/G feedstocks	18	31.6
Total	57	100

7. Compressor outages in ethylene plants with dual compressor trains occur twice as frequently as in plants with single trains.
8. An average of 98% of the material lost because of compressor outages is controlled by flares[2] operating within their smokeless capacities.

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[1] R. L. Standifer, IT Enviroscience, Ethylene (February 1981) (EPA/ESED report, Research Triangle Park, NC).

[2] V. Kalcevic, IT Enviroscience, Control Device Evaluation. Flares and the Use of Emissions as Fuel (in preparation for EPA, ESED, Research Triangle Park, NC).

II. ESTIMATED ANNUAL UPSET EMISSIONS FROM ETHYLENE-PLANT COMPRESSOR OUTAGES IN REGION 7 (HOUSTON AREA)

A. BASIS (SEE SECT. V)

1. Number of ethylene plant compressor outage incidents: 60 (see Table II-1).

2. Average material loss per incident for plant producing 1 billion lb of ethylene per year: single-train processes, 1.8 million lb; dual-train processes, 135,000 lb.

3. Average annual capacity (million lb of ethylene): plants using ethane/propane (E/P) feed, 513.6; plants using naphtha/gas-oil (N/G) feed, 1107.6.

4. Breakdown of number of single- vs dual-train plants; E/P vs N/G plants:

   E/P process plants, 68.4%.
   N/G process plants, 31.6%.
   E/P/ process plants, 50% with single trains; 50% with dual trains.
   N/G process plants - 90% with single trains; 10% with dual trains.

The above breakdown converts into the following values:

Single-train E/P plants: 0.5 X 68.4% = 34.2
Dual-train E/P plants: 0.5 X 68.4% = 34.2
Single-train N/G plants: 0.9 X 31.6% = 28.4
Dual-train N/G plants: 0.1 X 31.6% = 3.2
100%

B. CALCULATIONS

1. Breakdown of Compressor Outage Incidents

The following calculations are based on the assumption that the frequency of incidents in dual-train plant is twice that in single-train plants:

Single-train plants (E/P and N/G): 34.2 + 28.4 = 62.6%.
Dual-train plants (E/P and N/G): 34.2 + 3.2 = 37.4%.

Single-train plant incidents: $\frac{62.6}{62.6 + (2 \text{ X } 37.4)} = 45.6\%$

Dual-train plant incidents: $\frac{2 \text{ X } 37.4}{62.6 + (2 \text{ X } 37.4)} = 54.4\%$.

Number of single-train E/P plant incidents: $45.6\% \text{ X } \frac{34.2}{34.2 + 28.4} \text{ X }$ 60 incidents = 14.95.

Number of single-train N/G plant incidents: $45.6\% \text{ X } \frac{28.4}{34.2 + 28.4} \text{ X }$ 60 incidents = 12.41.

Number of dual-train E/P plant incidents: $54.4\% \text{ X } \frac{34.2}{34.2 + 3.2} \text{ X }$ 60 incidents = 29.85.

Number of dual-train N/G plant incidents: $54.4\% \text{ X } \frac{3.2}{34.2 + 3.2} \text{ X }$ 60 incidents = 2.79

Total 60.0

2. Estimated Material Losses

From single-train E/P plants: 14.95 incidents/yr X $1.8 \text{ X } 10^6$ lb lost/incident X $\frac{513.6 \text{ X } 10^{6\,a}}{1000 \text{ X } 10^{6\,b}} = 13.82 \text{ X } 10^6$ lb/yr

From dual-train E/P plants: 29.85 incidents/yr X $1.35 \text{ X } 10^5$ lb lost/incident X $\frac{513.6 \text{ X } 10^{6\,a}}{1000 \text{ X } 10^{6\,b}} = 2.07 \text{ X } 10^6$ lb/yr

From single-train N/G plants: 12.41 incidents/yr X $1.8 \text{ x } 10^6$ lb lost/incident X $\frac{1107.6 \text{ X } 10^{6\,a}}{1000 \text{ X } 10^{6\,b}} = 24.74 \text{ X } 10^6$ lb/yr

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[a] Average plant capacity (E/P--513.6 X 10^6 lb/yr, N/G--1107.6 X 10^6 lb/yr).
[b] Plant capacity basis for estimated material losses (1000 X 10^6 lb/yr).

From dual-train N/G plants: 2.79 incidents/yr X 1.35 X 10^5 lb

$$\text{lost incident} \times \frac{1107.6 \times 10^{6^a}}{1000 \times 10^{6^b}} = 0.42 \times 10^6 \text{ lb/yr}$$

Total annual material losses from ethylene plant compressor outages in TACB Region 7 = 41.05 X 10^6 lb/yr.

3. Estimates of VOC Emissions from Ethylene Plant Compressor Outages Based on 98% of VOC Material Losses Being Controlled by Flares and on 98% and 90% Flare Efficiencies[c]

At 98% flare efficiency: $41.05 \times 10^6 \times [0.02 + (0.98)(0.02)] = 1.625 \times 10^6$ lb/yr

At 90% flare efficiency: $41.05 \times 10^6 \times [0.02 + (0.98)(0.10)] = 4.844 \times 10^6$ lb/yr

III. ESTIMATED ANNUAL UPSET EMISSION FOR ENTIRE SOCMI INDUSTRY IN THE UNITED STATES

A. BASES

1. Upset emissions are proportional to production.
2. 50% of ethylene production is in TACB region 7.
3. 33.3% of other SOCMI production is in TACB region 7.
4. Flare efficiencies are 90 and 98%.[a]
5. 98% of ethylene plant compressor-outage losses are flared.
6. Upset losses from leaks are released without control.
7. 50% of all other losses from upsets are flared.
8. Estimated emissions in Table V-1 do not include flare inefficiencies.

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[c] Flare efficiencies have not been satisfactorily documented except for specific designs and operating conditions using standard fuels. Efficiencies used are for tentative comparison purposes.

B. CALCULATIONS

1. Total Annual Upset Emissions from Ethylene Plant Compressor Outages

At 98% flare efficiency: $\frac{1.625 \times 10^6 \text{ lb/yr}}{0.5} = 3.250 \times 10^6 \text{ lb/yr} = 3250 \text{ M lb/yr}$

At 90% flare efficiency: $\frac{4.844 \times 10^6 \text{ lb/yr}}{0.5} = 9.688 \times 10^6 \text{ lb/yr} = 9688 \text{ M lb/yr}$

2. Total Annual Upset Emissions from Major Leaks (See Table V-1)

$$\frac{131.1^{a} \text{ M lb}}{0.333} = 393 \text{ M lb/yr}$$

3. Total Annual Upset Emissions from All Other Sources[b]

Emissions not flared:

$$(648.5^{c} \text{ M lb} - 131.1^{d} \text{ M lb}) \times \frac{0.50^{e}}{0.333^{f}} = 776 \text{ M lb not flared}$$

Emissions from flares:

At 98% flare efficience——776 M lb X 0.02 = 15.5 M lb

At 90% flare efficience——776 M lb X 0.10 = 77.6 M lb

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[a] Includes ethylene plant emissions. The use of the general production factor (33.3%) for the total rather than the ethylene production factor (50%) for the respective portion of this minor source does not significantly affect the overall estimate.

[b] Includes all ethylene plant emissions except those resulting from compressor outages. The use of the general production factor (33.3%) rather than the ethylene production factor (50%) for the ethylene industry portion of these minor sources does not affect the overall estimate significantly.

[c] From Table V.

[d] From Table V.

[e] 50% not flared.

[f] General production factor (33.3% of total SOCMI production estimated to be in TACB Region 7).

4. Total Annual Upset Emissions from SOCMI

	98% Flare Efficiency	90% Flare Efficiency
Ethylene plant compressor outages	3250 M lb	9688 M lb
Major leaks	393 M lb	393 M lb
Other emissions not flared	776 M lb	776 M lb
Other emissions from flares	16 M lb	78 M lb
Total	4435 M lb	10935 M lb

IV. ESTIMATED IMPACT OF UPSET EMISSIONS ON TOTAL SOCMI EMISSIONS OF VOC

The total annual VOC emissions are estimated to be 1.5 X 10^9 lb (1979).[a] The estimated contribution of upset emissions is as follows:

(1) At 98% flare efficiency:

$$\frac{4.4 \text{ X } 10^6 \text{ lb/yr upset emissions}}{1.5 \text{ X } 10^9 \text{ lb/yr total emissions}} \text{ X } 100 = 0.29\%$$

(2) At 90% flare efficiency:

$$\frac{10.9 \text{ X } 10^6 \text{ lb/yr upset emissions}}{1.5 \text{ X } 10^9 \text{ lb/yr total emissions}} \text{ X } 100 = 0.73\%$$

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[a] Based on preliminary estimates of VOC emissions for the SOCMI made at the beginning of this program. Revised estimates, based on information obtained during the course of the program, will be included in a forthcoming summary report.